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TRW Systems Group, Redondo Beach, CA

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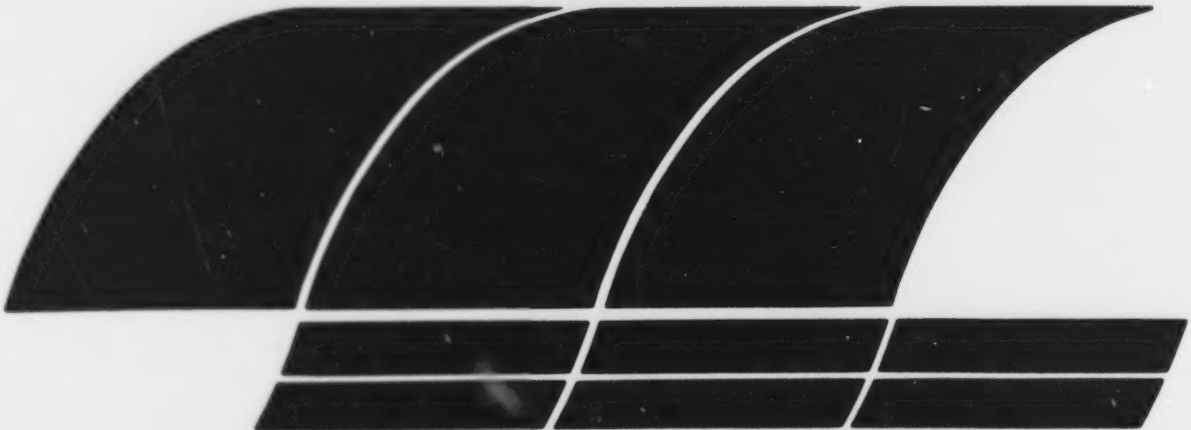

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PREFACE

These proceedings document the 26 presentations made at the Process Measurements for Environmental Assessment Symposium held February 13 - 15, 1978, at the Peachtree Plaza Hotel, Atlanta, Georgia. This Symposium was sponsored by the Process Measurements Branch of EPA's Industrial and Environmental Research Laboratory-Research Triangle Park, as Task 24 of EPA Contract Number 68-02-2165 to TRW Defense and Space Systems Group, Redondo Beach, California. The objective of this Symposium was to bring together people who were responsible for planning and implementing sampling and analysis programs for multi-media environmental assessment. The program consisted of sessions defining the uses of environmental assessment data, the techniques for acquiring information, and recent user's field experiences with environmental assessment measurement programs.

Mr. James A. Dorsey, Chief, Process Measurements Branch, was Symposium Chairman. The Welcoming Address was delivered by John K. Burchard, Director of Industrial Environmental Research Laboratory-RTP; the Keynote Paper was delivered by Dr. Stephen J. Gage, Assistant Administrator for Research and Development for the Environmental Protection Agency. The Symposium was organized and planned by Dr. Eugene A. Burns, who was employed by TRW Defense and Space Systems during the initial part of the project and finally by Systems, Science and Software during the last four months of the project activity. He was assisted by Mr. Charles T. Weekley of TRW who in turn had support services at the Symposium from M. A. McKay, L. Shober and M. W. Wong of TRW and B. Foil and S. Sharpe of EPA's IERL.

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PARTICIPATING EPA OFFICIALS AND SESSION CHAIRMEN

JAMES A. DORSEY
Symposium Chairman

Mr. Dorsey is Chief of the Process Measurements Branch in the EPA's Industrial Environmental Research Laboratory-RTP. He received his B.S. in Chemistry from Florida State University. He is responsible for integrated in-house/contract programs for the development and application of measurement procedures for energy and industrial processes. Prior to joining EPA in 1964, Jim was employed by Shell Oil Company as a research chemist. He has over 20 years of experience developing sampling and analysis techniques using advanced methods of instrumental analysis. Current studies include the sampling and analysis of organic and inorganic trace materials in gas, liquid and solid feed, product and waste streams. Jim is a member of the American Chemical Society and the Air Pollution Control Association.

JOHN K. BURCHARD
Welcoming Address

Dr. Burchard is the Director of the Industrial Environmental Research Laboratory-RTP. He is responsible for the management of programs to develop and demonstrate cost-effective technologies to prevent, control, or abate pollution from industrial operations involving energy and mineral resources. He was recently appointed as senior ORD Official for EPA's Environmental Research Center in Research Triangle Park, N.C. Since joining EPA in 1970, he has served in several capacities - as Chief of the Laboratory's Technical Analysis Section, Chief of the Development Engineering Branch, and Assistant Director. Before joining EPA, Dr. Burchard worked in industry for 10 years. He holds B.S., M.S., and Ph.D. degrees in Chemical Engineering from Carnegie Tech.

STEPHEN J. GAGE
Keynote Address

Dr. Gage is Assistant Administrator for Research and Development for EPA. He is responsible for planning, directing and coordinating all Agency research activities covering air, water, toxic substances, radiation energy, pesticides and solid wastes. He joined EPA in 1974 as Acting Director of the Office of Energy Research; in 1975 he became the Deputy Administrator for Energy, Minerals and Industry. Prior to joining EPA, he was with the Council on Environmental Quality. During 1971-73, Dr. Gage was a White House Fellow. He joined the faculty at the University of Texas in 1965 and became Director of the Nuclear Reactor Laboratory in 1966. He received a B.S. in Mechanical Engineering from the University of Nebraska and M.S. and Ph.D. degrees from Purdue University.

ROBERT P. HANGEBRAUCK
Session Chairman

Mr. Hangebrauck is the Director of the Energy Assessment and Control Division at EPA's Industrial Environmental Research Laboratory. Mr. Hangebrauck received his B.S. from Cal-Tech in 1959. He has served with the EPA and its predecessor agencies for 17 years in various capacities, including Chief of the Clean Fuels and Energy Branch, Chief of the Demonstration Projects Branch, Control Systems Laboratory, and Assistant to the Director of the Bureau of Engineering and Physical Sciences. He is currently in charge of conducting the divisions' research and development programs to identify and control multimedia pollutants discharged in the environment from stationary sources.

LARRY JOHNSON
Session Chairman

Dr. Johnson is an Analytical Chemist in the Process Measurements Branch for EPA's Industrial Environmental Research Laboratory-RTP. He received his B.S. in Chemistry from Iowa State University and his Ph.D. in Chemistry from the University of Texas. Dr. Johnson manages contracts to develop screening procedures for environmental assessment programs and compound specific procedures for detailed analysis of complex samples from industrial processes. He is also responsible for evaluating the applicability of biological screening tests to complex effluent samples. He has specialized in the areas of organic sampling and analysis for trace components in industrial feed stocks and energy process effluents. Prior to joining EPA in 1972, Dr. Johnson was employed as an analytical chemist by PPG Industries and as a research chemist by Monsanto.

CHARLES H. LOCHMULLER
Session Chairman

Dr. Lochmuller is an Associate Professor of Chemistry with Duke University. He is a consultant to the EPA Industrial Environmental Research Laboratory/RTP Process Measurement Branch in the areas related to the development of analytical methodology for environmental assessment and a member of its advisory panel on organic analysis. Prof. Lochmuller was one of the originators of the staged sampling and analysis protocol for environmental assessment process measurements. He received his B.S. in Chemistry from Manhattan College and his M.S. and Ph.D. degrees in Analytical Chemistry from Fordam University. His research interests are in the area of fundamental aspects of the molecular basis for selectivity in chemical separation methods. His recent work includes areas of charged particle induced x-ray emission analysis and Fourier Transform Magnetic Resonance Spectroscopy.

EUGENE A. BURNS
Session Chairman

Dr. Burns is Manager of the Chemistry and Chemical Engineering Program for Systems, Science and Software (S^3). He received his B.A. in Chemistry from Pomona College and his Ph.D. in Analytical Chemistry from Massachusetts Institute of Technology. Over the past 25 years, he has held a variety of research and management positions. Prior to joining S^3, Dr. Burns was employed by TRW for 15 years. As Manager, Chemistry Department, one of his responsibilities was energy-related environmental processes including the development of sampling and analysis methodology for characterizing process streams. Previous experience includes Chief of the Chemistry Section, Jet Propulsion Laboratory; and Head of the Analytical Chemistry Section, Stanford Research Institute's Propulsion Services Division.

KARL J. BOMBAUGH
Session Chairman

Mr. Bombaugh is a Principal Scientist at Radian Corporation where he is responsible for the development of strategies and systems for environmental tests. He obtained his B.S. in Chemistry from Juniata College. Over the past thirty years, he has held a variety of positions in both research and management. His experience covers a broad range of analytical and process technology, including infrared spectrometry, both gas and liquid chromatography, and on-stream analysis. As Vice-president for Research and Development at Waters Associates, he directed a group who pioneered in the development of modern high pressure liquid chromatography. He has authored more than fifty publications including chapters in several books. He has served on the editorial advisory board of the *Journal of Chromatographic Science*, and the *Chemical Rubber Handbook of Chromatography*. He is now Chairman Emeritus of ASTM Committee E19 on Chromatography.

SESSION SPEAKERS

ENVIRONMENTAL ASSESSMENT OVERVIEW

SESSION I

RAYMOND D. COOPER

Dr. Cooper is Acting AD for Integrated Assessment in the Division of Regional Assessment for the Department of Energy. He received his B.S. in physics from the University of Illinois. Dr. Cooper has advance degrees in physics (M.S. and Ph.D.), from Iowa State Universtiy and Massachusetts Institute of Technology, respectively. Prior to assuming his present position, Dr. Cooper served as Assistant Director for Integrated Assessment in the Division of Technology Overview, Energy Research and Development Administration, and Program Manager at the U.S. Atomic Energy Commission for Radiological Physics in the Division of Biomedical and Environmental Research. Prior to this he did research for the U.S. Army on the effects of nuclear radiation, electron and gamma ray interactions, dosimetry, and application of electron accelerators to food irradiation. Before his work for the Federal Government, he taught physics at Tufts University.

RALPH M. PERHAC

Dr. Perhac is Program Manager, Environmental Assessment Department at the Electric Power Research Institute (EPRI). He received his A.B. from Columbia, A.M. from Cornell University, and his Ph.D. from the University of Michigan. Prior to joining EPRI, he was the Program Director for Environmental Effects of Energy for the National Science Foundation. Prior to that, he was a Consulting Researcher, Environmental Sciences Division at Oak Ridge National Laboratory. He was a professor of Geochemistry at the University of Tennessee for seven years after he left the Exxon Corporation where he was a Senior Research Geochemist.

ENVIRONMENTAL ASSESSMENT OVERVIEW

SESSION II

RICHARD G. RHOADS

Mr. Rhoads is Director of the Control Programs Development Division in the Environmental Protection Agency's Office of Air Quality Planning and Standards at the Research Triangle Park, North Carolina. He is responsible for developing national policy and guidance, and providing evaluations and assessing effectiveness, of the air pollution control programs under Section 110 and 111(d) of the Clean Air Act. Dick graduated from Rensselaer Polytechnic Institute in 1960. Prior to assuming his present position, Mr. Rhoads served in several other areas of the Environmental Protection Agency's air pollution control program. Prior to joining EPA, he conducted operations research, systems analysis, and aeronautical design studies for the Federal Government.

EUGENE E. BERKAU

Dr. Gene Berkau is Director, Industrial Pollution Control Division, Industrial Environmental Research Laboratory (IERL) Cincinnati, Ohio, U.S. Environmental Protection Agency. Gene's Division is responsible for sponsoring programs in research, development and demonstration of cost-effective technologies to control pollution from the manufacturing of industrial products. Dr. Berkau has advanced degrees in Chemical Engineering (M.S. and Ph.D.), from Vanderbilt University. He has been with EPA and its predecessor Agency since 1970. Prior to the current assignment, his EPA responsibilities were in research development and demonstration of control methods for noise and air pollution from combustion systems. Before joining the Federal Government, he was employed by the Monsanto Textile Division at the Chemstrand Research Center, Research Triangle Park, North Carolina.

THOMAS W. HUGHES

Mr. Hughes is a Research Group Leader at Monsanto Research Corporation. Tom received his B.S. in Chemical Engineering from the University of Cincinnati in 1973. He has been involved in Environmental Assessment studies for EPA at Monsanto Research Corporation since 1974. He has been performing Source Assessment studies for IERL in the organic chemicals and product areas. Tom has also been involved in control technology development for both criteria pollutants and toxic substances in air and water media. The Source Assessment studies that Tom discussed constitute one of the first major EPA programs involving comprehensive pollutant assessment of source emissions.

SHAHBEG S. SANDHU

Dr. Sandhu is a Research Biologist for Health Effects Research Laboratory, Environmental Protection Agency, Research Triangle Park, North Carolina. He received his B.S. and M.S. from Punjab University, India. He received his Ph.D. from Purdue University in 1968. Prior to joining EPA, he was Professor of genetics at North Carolina Central University. His major research areas are mammalian cell culture, mutagenetics and plant genetics. Dr. Sandhu is presently assisting the IERL on programs for the application of bioassay tests to industrial samples.

KENNETH M. DUKE

Dr. Duke is Associate Manager, Ecology and Ecosystems Analysis Section, Battelle Columbus Laboratory. He received his B.S. in Zoology and Entomology (1966) at Brigham Young University; his M.S. in Zoology and Entomology (1968), from Brigham Young University, and his Ph.D. in Entomology (1971) from the University of Georgia. He is currently the leader of a program designed to assist the U.S. Environmental Protection Agency in developing a protocol of bioassays to screen various gaseous, liquid, and solid industrial effluents for their toxicity.

MEASUREMENT TECHNOLOGIES

SESSION I

DAVID E. BLAKE

Mr. Blake is the Manager, Industrial and Environmental Engineering Department, Aerotherm Division of Acurex Corporation. Mr. Blake obtained his B.S. in Chemical Engineering at California State University at San Jose in 1965. He worked for seven years at Stanford Research Institute and three years at Electro Print, Inc. before joining Acurex in 1975. At Acurex, Mr. Blake has managed a number of projects primarily in the areas of environmental instrumentation and development of coal conversion processes. He was the Program Manager for the SASS design and development program which was conducted for the Process Measurements Branch.

FRANKLIN SMITH

Mr. Frank Smith has been an engineer on the technical staff of the Research Triangle Institute since 1970. His primary areas of work have been in the development and application of quality assurance techniques to air pollution and measurement systems and networks. He received a B.S. in mathematics from Arkansas State University in 1959 and an M.S.T. in physical sciences from the University of Missouri in 1964. Prior to 1970, Mr. Smith was employed as a physicist at the Naval Weapons Laboratory, Dahlgren, Virginia, where he was concerned with the effects of electromagnetic radiation on various ordnance items.

RAY F. MADDALONE

Dr. Maddalone is Head of the Environmental and Process Chemistry Section at TRW Defense and Space Systems. He is Manager of the Reduced and Oxidized Inorganic Emissions Term Form Level-of-Effort Program sponsored by EPA-IERL/RTP. He received his B.S. in Chemistry from Notre Dame in 1970 and his Ph.D. in Analytical Chemistry from Louisiana State University in 1974. Ray is a specialist in SO_2/SO_3 emission measurements.

PHILIP L. LEVINS

Dr. Levins is Leader of the Analytical Chemistry Unit at Arthur D. Little, Inc. He has directed several experimental programs whose focus has been on problem definition and method development concerning organic species in the environment. Among these is the present organics measurement program for EPA, development of sampling and analysis methods for industrial hygiene studies and determination of the chemical odor species in diesel exhaust. He received his B.S. in Chemistry from the University of Vermont and Ph.D. in Physical Organic Chemistry from the University of New Hampshire.

PETER W. JONES

Dr. Jones is Associate Manager of the Organic, Analytical and Environmental Chemistry Section, Battelle Columbus Laboratories. His principal responsibilities have been to initiate and direct hazardous ambient and stack gas pollutants. Dr. Jones received his B.S. in Chemistry and Physics in 1966 from Hatfield College of Technology, Hatfordshire, England, and his Ph.D. in Chemistry from the University of York, Yorkshire, England in 1969. Prior to joining Battelle in 1971, he was a post-doctoral fellow at the University of Manitoba. Dr. Jones is a specialist in sampling and analysis of trace organic emissions from industrial and energy processes.

MEASUREMENT TECHNOLOGIES

SESSION II

HENRY J. KOLNSBERG

Mr. Kolnsberg is a Senior Project Manager with TRC — The Research Corporation of New England in Wethersfield, Connecticut, where he is responsible for contracts to develop fugitive emissions measurement techniques and to provide environmental consulting services to a variety of clients. A mechanical engineering graduate of The Cooper Union, he received his M.B.A. in Management from the University of Connecticut.

WILLIAM A. TELLIARD

Bill Telliard is Chief of the Energy and Mining Branch within the Effluent Guidelines Division of the Office of Water and Hazardous Materials, the Environmental Protection Agency. He attended Kent State University and Western Reserve where he received his Masters Degree in chemistry. Among his major responsibilities is the analytical chemistry phase of the current BAT review projects. In this role, Bill handles the development and updating of sampling and analytical protocols, as well as validation procedures appropriate to each of the 21 industrial studies.

CHARLES M. SPARACINO

Dr. Sparacino received his Ph.D. in Organic Chemistry from Emory University in 1969. He spent a year as a postdoctoral fellow at the Worcester Foundation for Experimental Biology in Massachusetts, studying biogenetic problems relating to steroidal terpenes. After joining the Research Triangle Institute in 1970, Dr. Sparacino has been involved in drug synthesis and metabolism studies, and more recently, in programs involving environmental problems. These programs include method development for coal gasification byproducts and air particulate and vapor analysis.

DAVID F.S. NATUSCH

Dr. Natusch is Professor of Chemistry and Acting Chairman of the Chemistry Department at Colorado State University. He obtained his B.S. and M.S. degrees from the University of Canterbury in New Zealand and his Doctorate as a Rhodes Scholar at Oxford University in Britain. He has worked as a research scientist for the New Zealand Department of Scientific and Industrial Research in the areas of air pollution and geothermal power production. Most recent, he was Associate Professor of Environmental Chemistry at the University of Illinois. His research involves the development and application of instrumentation for the detailed characterization of environmental pollutants and energy process stream materials and the investigation of the physical and chemical behavior of such materials.

INDUSTRIAL PROCESS APPLICATIONS

DONALD D. ROSEBROOK

Don Rosebrook is a Program Manager at Radian Corporation. He received his B.S. in Chemical Engineering from Purdue in 1958 and a Ph.D. in Analytical Chemistry from Kansas State in 1964. He began his professional career at the Midwest Research Institute where he was primarily involved in trace analysis, development of sampling approaches for trace organics in all media, gas chromatography-mass spectrometry. He joined Syracuse Research Corporation in 1972 where he was Manager, Analytical Services. Since 1975, he has been with the Radian Corporation where he started the Organic Chemistry Department, primarily involved in trace analysis and programs dealing with refining and coal conversion.

GARY D. RAWLINGS

Dr. Rawlings is a Senior Research Engineer at the Monsanto Research Corporation. He is currently the Project Leader of a special source assessment project designed to evaluate the toxicity of textile mill waste waters. He received his B.S. in Physics in 1970 and his M.S. in Nuclear Physics in 1971, both at Southwest Texas State University. He received his Ph.D. in Environmental Engineering in 1974 at Texas A&M University. Dr. Rawlings has had wide industrial experience in assessing the potential environmental impact of several industries in support of an EPA contract entitled "Source Assessment."

J. WARREN HAMERSMA

Dr. Hamersma is a staff engineer for environmental projects in the Chemistry Department of TRW Defense and Space Systems. He received his B.S. in Chemistry from Calvin College and his Ph.D. in Physical Organic Chemistry from the University of Connecticut. He is presently in charge of the laboratory operations for the Environmental Assessment of Conventional Combustion Systems Program. Dr. Hamersma was manager for EPA-funded tasks to develop and integrate the phased (Level 1 and Level 2) environmental assessment sampling and analytical strategy and to document procedures for Level 1 sampling and analysis. Prior to joining TRW, he had eight years in quality control and organic analysis experience at International Chemical and Nuclear Corporation and at Arco Chemical Corporation.

RICHARD L. MEEK

Dr. Meek is Head, Chemical Process Section of Southern Research Institute, Birmingham, Alabama. He received his Ph.D. in Chemical Engineering from Georgia Tech in 1952. Dr. Meek is currently working on a program to evaluate control systems in the nonferrous metals industry sponsored by EPA's Cincinnati Industrial Environmental Research Laboratory. Prior to joining Southern Research Institute, he was with the Cities Service Company as Research Coordinator and Assistant Director, Research and Development for Cities Services Chemicals and Metals Division.

CHARLES H. DARVIN

Mr. Darvin is Program Manager for Metal Finishing Industries and Miscellaneous Industries Program for the EPA Industrial Environmental Research Laboratory, Cincinnati, Ohio. His assignments include the development of the laboratory research programs for these industries. His education includes a B.S. degree in Mechanical Engineering from the University of Evansville, Evansville, Indiana, and graduate work in Applied Mathematics and Business. His previous employment includes assignment to the Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, where he was the standards development engineer for the lead and zinc industries.

ENERGY PROCESS APPLICATIONS

K.S. MURTHY

Kesh Murthy is a Senior Engineer of the Energy and Environmental Process Department of Battelle Columbus Laboratories. He is currently the Deputy Program Manager of the ongoing program of environmental assessment of the fluidized-bed combustion process. Mr. Murthy received his

B.S. in Chemistry, Physics and Mathematics in 1958 from the University of Mysore, India; his B.S. in Chemical Engineering in 1966 from the Indian Institute of Chemical Engineers, Calcutta, India; and his M.S. in Environmental Engineering in 1973 from the University of Cincinnati. At Battelle, Mr. Murthy has focused on many research projects involving energy processes and their environmental interaction.

L.J. ANASTASIA

Lou Anastasia joined the staff of the Institute of Gas Technology in 1973. He is currently Manager of Environmental Engineering at the HYGAS Pilot Plant where he is responsible for the environmental assessment of the HYGAS Process and plant pollution control. He received his B.S. and M.S. degrees in Chemical Engineering from Purdue University. Previously, Lou was associated with Argonne National Laboratories where his 15 years of experience included studies on fluidized-bed combustion of coal, pyrochemical reprocessing of spent nuclear fuel, safety aspects for lithium-sulfur batteries for automobile propulsion, and fluidized-bed fluoride volatility reprocessing of spent nuclear fuel.

A.G. SHARKEY, JR.

A.G. "Jack" Sharkey is Manager of the Chemical and Instrumental Analysis Division of the Pittsburgh Energy Research Center. He is also Adjunct Associate Professor and Member of the Graduate Faculty, Earth and Planetary Science Department, University of Pittsburgh. He received his A.B. in 1941 from the College of Wooster and his M.S. from Case Institute of Technology in 1943. After three years of employment at Westinghouse Research Laboratories, he was employed by the Bureau of Mines and now the Pittsburgh Energy Research Center for the past 31 years. His major research interests are numerous but he has focused on the application of spectral analysis techniques to coal and coal-derived fuels. He has over 200 papers in the area of analysis of coal, coal-derived fuels and mass spectrometry instrumentation.

JACK E. COTTER

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KEYNOTE ADDRESS

PROCESS MEASUREMENTS
FOR
ENVIRONMENTAL ASSESSMENT

by

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In the beginning, environmental assessment was a whole lot easier. When the cave man stuck his head out of his cave, he could tell immediately whether a forest fire had polluted the air during the night. His keen senses could also detect the carrion that might be polluting his water supply—the stream that ran down the valley. But then again, he lost the major share of his family to mysterious and unknown causes.

Only in modern times have we been able to determine the causes of most of the afflictions which killed or debilitated the cave man's family. We've made the most progress in identifying and controlling germs or bacteria with unbelievable success in essentially stopping plagues, smallpox, tuberculosis, and diptheria, to name a few. We've made some important progress in identifying viruses, less so in controlling them. Unfortunately, we probably communicate the common cold from one to another—and suffer the consequences—in the same way the cave man did, the many commercial palliatives notwithstanding.

Our progress in identifying and controlling man-made chemicals in the environment has also been mixed. But then again, the general dispersion of toxic chemicals in the environment has only occurred seriously since the Industrial Revolution. In fact, most of the environmental chemicals we fear today have come into production only after World War II.

Certainly one of the earlier manifestations of man-made environmental problems, probably predating the Bronze Age, was lead poisoning from clay pottery. The naturally occurring lead salts leached from the clay pot had slow, cummulative effects on the early technologist and his family as he used his wits to superimpose his will on a harsh environment. But, in that act of shaping the environment to satisfy his needs, he had simultaneously concentrated a dilute toxic chemical and increased his exposure to that chemical. A nice lesson from primitive technology, isn't it.

Now, we recognize the threat of heavy metals like lead, cadmium, arsenic, and mercury, although we're not sure what control levels and methods to specify in all cases. We are less sure about the nature of the threat from toxic organic chemicals, intentionally or accidentally introduced into the environment. We are much less sure of what to do in many instances.

The threat from synthetic chemicals appears to be very general. The discovery of many man-made toxic chemicals, some of which were known cancer-causing agents, in New Orleans' drinking water several years ago was extremely sobering. Since then, analysis of the drinking water supplies of one hundred American cities indicated that a number of the cities sampled might have contamination problems with such exotic chemicals as tetrachloroethylene, pentachlorophenol bis-(2-chloroisopropyl) ether, and 3,4-benzofluoranthene. Fortunately, treatment techniques, such as activated carbon filtration, may remove most of these.

Of even greater concern are those situations where the chemicals have become widely dispersed in the environment before we knew it was happening, where the chemicals resist transformation into nontoxic products or do transform into very toxic materials, and where the chemicals or their products will continue to expose man or part of his food chain for years to come. DDT throughout the world, PCB's in the bottom of the Hudson River, kepone in the bottom of the James River—these are examples of where industrial activities have made perhaps an irreversible impact on the environment.

This is where Environmental Assessment comes in. We've learned a lot about the threats of pollution coming out of industrial air, water, and residual waste streams in the last few years. But, we want to do all we can to avoid being surprised by the DDT-, PCB-, and kepone—like disasters of the future.

If we are to keep the Nation's economy growing, that growth will depend in large measure on industrial expansion. To keep industry from fouling its nest and ours as well, we must know what is in industrial products, by-products, and wastes and must act to protect us and the environment, even while allowing industry to grow.

But, Environmental Assessment is no easy task. For the past three years we have been systematically measuring, with as much precision as possible, what and how much are being emitted by many industrial, especially energy processing, technologies. We have found that the major components of the products, by-products and waste streams are generally well-characterized. But with increasing concern over trace level contaminants and their subtle, cumulative effects on human health, we have been faced with increasingly difficult assessment problems.

The difficulty of obtaining representative samples from process streams which are at high temperature and pressure, which involve two- or even three-phase flow, and which often include other highly reactive chemical species, is immense. Chemically analyzing complex mixtures of chemicals, especially to trace contaminant levels, is the next tremendous challenge, even with today's powerful analytical chemistry techniques.

Once the emissions are chemically characterized, determination of the relative degree of health or environmental risk is the next painstaking step. This activity is particularly vexing when the long-term cumulative effects, such as those which might result from exposure to carcinogenic, mutagenic, or teratogenic agents are considered.

The fourth step, required when the preliminary screening results give strong evidence of toxicological or other hazards, is to conduct health effects studies of the waste streams or at least of their most hazardous components. This step is beyond the scope of Environmental Assessment as we usually define it. Similarly, the fifth step, identification of methods to control the substance, usually follows the Environmental Assessment.

The emergence of the Environment Assessment Program as a distinct and important part of EPA's environmental research efforts over the past several years is an excellent example of how the Agency's efforts have turned from primarily research in reaction to known environmental problems to include research which anticipates and tries to avoid future environmental problems. This change of emphasis also predated the rechartering of EPA's position toward toxics.

One of the best examples of these efforts has been in the area of chemical processing of coal. As we all know, the United States is going to have to use much more coal if our economy is to grow and our national security is not to be seriously compromised. Part of the coal will probably have to be converted to clean liquids and gases if the multiplicity of U.S. fuel needs are to be met. During the conversion process, coal is typically treated with hydrogen in one form or another to increase the ratio of hydrogen-to-carbon atoms in the resulting products. Because of the complex chemistry of coal and the economic necessity to hydrogenate only as far as required to make the desired product, the conversion process produces hundreds of different hydrocarbon compounds as by-products. Some of these by-products end up as trace contaminants in the products, others are emitted in fugitive emissions, and still others end up in residuum from the process. Even though these compounds may exist only at trace levels, they may present a serious health risk to plant workers or to the general public. Our Environmental Assessment activities have made considerable progress in identifying and quantifying many of these by-product materials. More will be made in the near future.

During the past decade, there has been a subtle but definite shift in our approach to environmental protection. We have moved steadily away from doing barely enough to protect public health and safety and toward doing as much as is practicable. In other words, we are beginning to use as much control technology as we can economically tolerate in order to have some margin of safety and flexibility for the future.

In 1970, the modified Clean Air Act established the requirement for New Source Performance Standards, necessitating the best commercially demonstrated pollution control equipment for certain air pollutants on all major new industrial facilities. In 1972, Amendments to the Federal Water Pollution Control Act established a system of effluent guidelines for the Best Practical Technology (BPT) and Best

Available Technology (BAT) for control of the most common water pollutants for each major industrial category. Last year the Environmental Protection Agency was ordered by a U. S. district court to apply, on an accelerated schedule, Best Available Technology standards to the control of 65 toxic materials in the wastewaters from 21 priority industries. Finally, six months ago the House of Representatives voted to require best available control technology on all new utility boilers in order to minimize the atmospheric loading of sulfur oxides and their by-products, to increase the use of locally available coals, and to give some room for industrial growth in most parts of the country.

In short, we are beginning to control air and water pollution wherever and whenever it can be controlled. And the scientific information on health and ecological effects of such pollution has consistently supported the wisdom of this trend.

Although we recognize the importance of environmental protection afforded by investments in control technology, there still linger ambivalent feelings about environmental control technologies. Do we really need them? Aren't there other ways of achieving the same objectives? Aren't there breakthroughs waiting just around the corner which will obviate the need of our control technologies? Or, if we shut our eyes tight and wish very hard, won't the problems go away? My answer is that control technologies are our bridge, and our only bridge, into an uncertain future.

Hence, there is no longer any question whether, or how far, we will compromise our environmental goals to achieve expanded energy resources and industrial growth. There need be no compromise. There shall be no articifical dichotomy of energy and industrial growth versus environmental protection. We will have the growth we need, and it will not be at the cost of our property, our health, or our sense of aesthetics. This is President Carter's policy.

With this in mind, we have been accelerating the development of controls for four of the major problems, three of them air pollutants—sulfur oxides, nitrogen oxides, and fine particles—and the fourth—mining disruption. While our technology bridge to the future over each of these problems is far from perfect, at least we can now see the other shore.

As I mentioned earlier, we are also looking into the future to assure that advanced technologies, when they do become commercially applied, do not pose their own set of environmental hazards. It would be a distorted perspective to limit our attention to solving today's problems while allowing tomorrow's to grow unchecked. For example, in parallel with efforts by the Department of Energy to develop coal-fired fluidized bed combustors for heat, steam, and power generation, EPA is conducting a complete environmental characterization of these processes. Our goal is to help to avoid any potential environmental problems that may be associated with this very promising technology. On Wednesday, you will be given a description of the scope and preliminary findings of this effort.

Synthetic fuels, as I have indicated, also offer solutions to problems associated with the use of coal, but may present some new, and potentially serious, environmental threat. Working with DOE, we will be monitoring the Country's early synthetic fuels plants, as they become operational within the next few years. Such efforts will help assure that the best controls are available at the lowest costs and at the right time so we can meet our needs for alternative supplies of liquid and gaseous fuels. The details on these efforts will also be presented in a session on Wednesday.

Since the initiation of EPA's Environmental Assessment Program three years ago, much progress has been made in developing adequate sampling and analytical techniques. Such technology is evolutionary in nature, in that we improve on the techniques as we get experience in their application and as we attempt more complex sampling and analysis. The people involved in these efforts have a right to be proud of their accomplishments. You who have been involved in these efforts will hear about them on Tuesday. There still, however, are significant challenges for improvements in methods, specifically selectivity, sensitivity, accuracy, and lower cost.

This symposium provides an important formum for those applied researchers who are developing and using process measurements for environmental assessments to exchange ideas. Your findings and accomplishments will continue to guide the Environmental Assessment Program so that we can assure that the Nation's energy and industrial processes will meet our present and future environmental control requirements.

THE DOE INTEGRATED ASSESSMENT PROGRAMS

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Abstract

The Integrated Environmental Assessment programs of DOE are designed to support the Assistant Secretary for the Environment in the conduct of his responsibilities. In order to fulfill these responsibilities, particularly those associated with policy guidance for the Department, there are three kinds of assessment activities which must be carried out. Since the Department is responsible for developing a national energy policy, national environmental assessments of this policy are required. Technology assessments must be done in order to explore environmental issues which affect technology development decisions and the levels of environmental control required. Finally, regional environmental assessments must be carried out because environmental and social impacts of energy policies and technological developments are very dependent upon the specific characteristics of the region involved. Examples of all three types of assessment were recently completed in connection with the National Energy Plan as submitted to Congress. A national assessment of the environmental impacts associated with the plan was made using a comprehensive simulation model based on the SEAS system calibrated to the NEP assumptions for the period 1975 to 2000. Regional assessments were made of the impact of the plan on New England and on Region VI where conversion from oil and gas to coal is expected. Finally, technology assessments were made of the prospects for solar energy and of the impacts of the coal solid waste, and local socioeconomic well-being.

Introduction

The Department of Energy has broader responsibilities than its predecessor agencies and the Integrated Assessment Program under the Assistant Secretary for Environment has also changed and broadened its scope. The assessments supported under this program are aimed at three types of policy questions which basically determine the different thrusts of the studies. First, there is a need to review and assess *national* energy policies and strategies for environmental impact. This will assist in the development of a national energy policy which is environmentally acceptable. Secondly, there is a need to assess the health, environmental, and social impacts of new *technologies* being developed by DOE. These technology assessments will provide guidance on the rate and direction that development should take and the environmental controls which must be built in. Finally, since most impacts on the environment as well as on man's social well-being are local, it is necessary to do *regional* assessments of the impacts of alternative future energy strategies. This will provide analyses of regional issues which must be taken into account in national energy planning as well as providing options for mitigating regional impacts and removing constraints to further energy development.

These three kinds of assessments are not mutually exclusive but, in fact, often overlap in any particular study. For example, a National Coal Utilization Assessment now being completed is a regional study of the environmental effects of increased coal use which will be integrated into a national picture. An assessment of the impacts of geothermal development in the Imperial Valley of California is both a study of the technology and the region. Future studies, however, are expected to fall more clearly in one of the three categories because of the questions which are being asked of the assessments.

The data and information needs of the three types of assessments differ. The national assessments will be done annually using a series of models which calculate energy residuals by region after a disaggregation based on economic activity. Since the models do not yet calculate impacts on ecosystems or health effects, the level of sophistication of the data need not be as high as in the other two types of analyses. The technology assessments require the best physical and chemical characterization which can be made of the effluents from each part of the fuel cycle. It is here that much better information is needed. The regional assessments also require careful measurements of the present environment so that calcuation of impacts of future energy options can be made.

A National Assessment of the President's Energy Plan

The first Annual Environmental Assessment Report has been completed to determine the impacts of the National Energy Plan on the environment and to compare this to a base case scenario without the NEP initiatives. The analysis was made to determine if there are potential environmental problems associated with the plan, to develop the methodology for an annual update of the analysis, and to assist in setting environmental research priorities.

A large part of the input information used in this type of assessment consists of economic and demographic assumptions. The principal energy and environmental data developed included residual data on a national and regional level and cost data on pollution abatement for both energy and nonenergy supply technologies. Residuals and abatement costs associated with industrial, transportation, commercial and residential demand activities were also used. Data bases for energy supply sectors such as those collected by Hittman Associates, Teknekron, EPA, etc., formed the basis for the residuals analysis.

The results of this assessment included the identification of a number of key environmental issues and the regions where these issues are of primary concern. Figure 1 shows how SO_x emissions vary in several regions between 1975 and 2000 based on the two scenarios. In general, the NEP scenarios is seen to result in smaller SO_x emissions because of the increased conservation component. Figure 2 shows the water consumption by energy technology according to NEP and pre-NEP scenarios, 1975, 1985, and 2000. This indicates clearly the very large increase in the use of water for energy by the year 2000.

The requirements for new measurements and much more sophisticated data in this type of analysis are less than in the other kinds of assessments to be described here. The modeling techniques used and the questions being asked of the analysis make it unnecessary to know energy emissions in detail much beyond the criteria pollutants. As experience is gained with the national assessments, more data of the kind needed in the technology and regional assessments will be required.

Technology Assessment

The second major type of assessment carried out under the Assistant Secretary for Environment, DOE, is a technological assessment. These studies are principally concerned with new technologies being developed by the agency but include an analysis of impacts of the present and possible future installed energy industry.

There are three major uses within DOE for these technology assessments. First, they are used to identify present and future environmental control needs. In order to help specify future environmental controls, needed environmental and health research and development is identified by these assessments. Finally, they are used as input for both technology development planning and environmental development planning.

The data and information needs for a technology assessment are much more sophisticated than for the national assessment described above. Even though the technology is still being developed, it is necessary to characterize the fuel cycle. The physical and chemical characteristics of the residuals from each element of the fuel cycle must be obtained either by measurement or from theory. Finally, the transport and fate of the effluents within the environment must be understood.

As an example of a technology assessment, the atmospheric fludized bed combustion of coal will be described. This study was done approximately one year ago, so the numbers shown should not be considered representative of our present knowledge.

Figure 3 shows the different elements involved in atmospheric FBC and the streams connecting the elements and the external environment. The effluent streams are listed in Table 1 since these will be responsible for the principal environmental impacts. Resource use (land, water, etc.) must be considered in addition to the effluents.

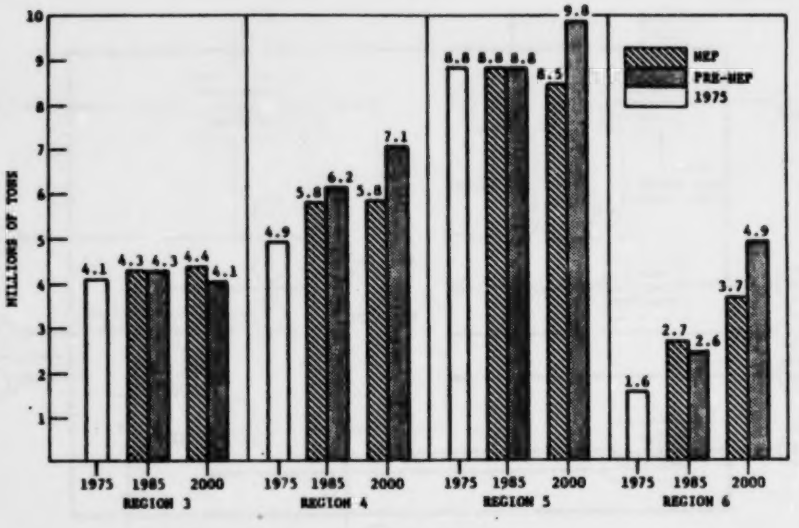

FIGURE 1. COMPARISON OF SO_x EMISSIONS BETWEEN THE NEP AND PRE-NEP SCENARIOS (FOR SELECTED REGIONS)

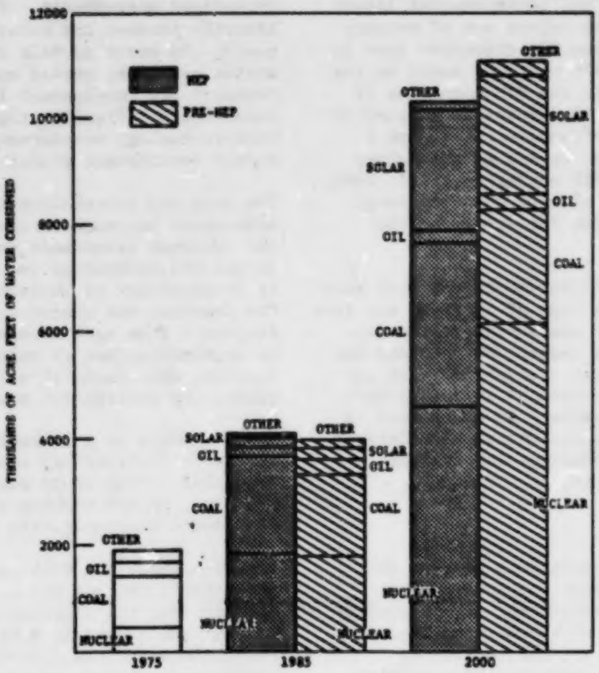

FIGURE 2. WATER CONSUMPTION BY ENERGY TECHNOLOGY ACCORDING TO NEP AND PRE-NEP SCENARIOS, 1975, 1985, and 2000

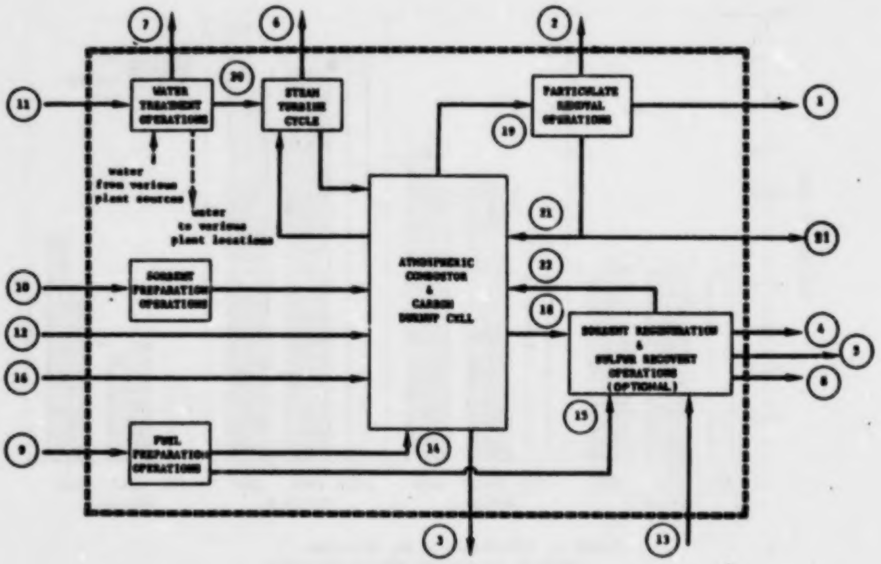
7
6
2
20
11
WATER TREATMENT OPERATIONS
STEAM TURBINE CYCLE
PARTICULATE REMOVAL OPERATIONS
1
19
water from various plant sources
water to various plant locations
21
21
22
ATMOSPHERIC COMBUSTOR & CARBON BURNUP CELL
10
SORBENT PREPARATION OPERATIONS
18
12
SORBENT REGENERATION & SULFUR RECOVERY OPERATIONS (OPTIONAL)
4
5
8
16
15
9
FUEL PREPARATION OPERATIONS
14
3
13

FIGURE 3. ATMOSPHERIC FBC OF COAL

TABLE 1

EFFLUENT STREAM DESIGNATIONS
ATMOSPHERIC AND PRESSURIZED FBC

STREAM NO.	DESIGNATION
1	Stack Gas
2	Particulate Removal Discard
3	Bed Solids Discard
4	Particulate Removal Discard—Regeneration Operations
5	Other Effluents from Regeneration and Sulfur Recovery Operations
6	Blowdowns from Steam Turbine Cycle
7	Blowdown from Water Treatment Operations
8	Product from Sulfur Recovery (Sulfur or Sulfuric Acid)
21	High Carbon Ash from Particulate Removal (recycle or alternate combustor)

Table 2 lists the trace metal discharges from fluidized bed combustion and from flue gas desulfurization. At the time that this assessment was done, there was no data on trace elements from FBC, so these are listed as unknown.

Table 3 lists the waterborne effluents discharged per day by a 500 megawatt fluidized bed combustion unit and by a similar conventional combustion plant with flue gas desulfurization, each operating at 75 percent load factor. The FBC unit is seen to have, in general, a lower release of effluents. Table 4 shows the results of the calcuation of public health impacts for a 1000 megawatt electric plant using fluidized bed combustion. Three different analytical models were used: 1) assuming new source performance standards in SO_2 and particulates, 2) in particulates alone and finally, 3) in a conventional combustion plant with a FGD unit attached.

From this kind of technology assessment, several research needs become apparent. For example, the following questions regarding trace elements must be answered:

1) Are all elements present in the coal emitted into the effluent streams?

2) What are the portioning factors for the elements?

3) What is the chemical form of the emitted element?

4) Is the deposition pattern different from that in conventional combustion and with FGD?

Questions associated with the waste product from FBC units can take the following forms:

1) What chemical form of the trace and major elements end up in the fly ash, in the bottom ash and in the slag?

2) What trace elements are aborbed on the spent sorbent?

3) How effective are the settling pool liners?

4) What reclamation procedures can be used for the waste ponds?

5) What are the environmental effects of ash used in roads and building materials?

Finally, looking at the calculated health effects we see a number of further questions which are raised by this assessment. These include the following:

1) What is the composition and chemistry of the effluent stream from the stack?

2) What atmospheric chemistry takes place after the release of the effluents?

3) Are there synergistic effects between the effluents and other materials in the environment?

4) Finally, what are the damage functions of the principal effluents from FBC units?

All of these questions will result in further research and development, the outcome of which will feed into improved technological assessments. The final results are used to set research priorities for environmental studies and development priorities for both the technology and the environmental control system associated with it.

Regional Assessments

The final type of assessment activity carried out under the environmental office of the Department of Energy is the regional assessment. These are conducted to characterize the environmental issues associated with the future energy supply and demand within a region. A regional entity will include a river basin, an electric power pool, or a political unit such as a state or county.

The principal purposes of these regional assessments are to obtain a regional perspective on the issues associated with national policy such as the National Energy Plan. In addition, they are a

TABLE 2

Trace Metal Discharges, FBC and FGD

Pollutant	Discharges, lb/day	
	FBC	Conventional
Al	U	1.2
Mn	U	0.05
Cd	U	0.01
Se	U	0.05
As	U	0.01
B	U	0.05
Pb	U	0.01
Ba	U	0.07

U = Unknown

TABLE 3

Waterborne Effluents, FBC and FGD

Element	Discharges, lb/day	
	5000MW FBC, 75% Load Factor	500-MW Conventional, 75% Load Factor
TSS	93 max 28 avg	189 max 57 avg
Oil and grease	19 max 14 avg	38 max 28 avg
Ammonia nitrogen	0.92	1.4
Nitrate nitrogen	0.17	1.2
Chloride	91	127
f.a. Chlorine	9.2 max 3.5 avg	9.2 max 3.5 avg
Sulfate	133	270
Fe	20	21
Cu	4.8	4.8
Zn	0.44	0.47
Cr	0.60	0.62
P	4.8	4.8
Na	67	143
Ni	4.8	4.8
Mg	106	116.0

TABLE 4

Results From the Public Health Impact Analysis for a 1000-MWe Plant

		Average Values for 50-mile-radius Circle				Highly Impacted Subarea			
		Expectation of life (e_0)		Deaths/10^6		e_0		Deaths/10^6	
		M	F	M	F	M	F	M	F
Baseline Values (Berkshire Co., Mass., White Population, 1970)		68.861	75.541	11,583	10,705	Same			
Model	**Assumption**								
A	NSPS in SO_2, TSP	68.851	75.529	5	6	68.830	75.510	16	15
B	NSPS in TSP	68.847	75.528	7	6	68.734	75.422	64	55
C	Conventional Combustion, FGD 1000 μg/10^6 Btu POM[a]	No detectable difference from baseline				68.860	75.541	1	0
C	AFBC, 3000 μg/10^6 Btu POM[a]	68.860	75.541	1	0	68.848	75.538	7	1

[a] Polycyclic Organic Material.

means to surface the state and regional environmental concerns which can have an impact on the implementation of national energy and environmental policies.

The regional assessments compare or balance the competing energy technologies and resources which can be utilized in a given region. The various technological options available in the near term and in the future are carefully considered and distributed in order to minimize environmental impacts on the region.

These assessments are used primarily to assist national energy planners to develop environmental and energy policies which will be acceptable within the different regions of the country. Regional assessments are designed to compliment the technology assessments and thereby provide the analytical support required for making policy choices at all levels of governmental energy and environmental planning.

The data and information required in a regional assessment is generally of two types. First, it is necessary to know the supply and demand picture of the region. This includes a knowledge of the future energy options which are available. The second major type of information required is a baseline characterization of the environment of the region. The kinds of ecosystems, the distribution of people, the distribution of natural resources and water resources within a region are all important in the analysis of future options and the environmental concerns which will be generated.

The results of a regional assessment are often given in terms of issues of concern to the region which are raised by a certain policy or a particular scenario. For example, an analysis of the impacts of the National Energy Plan on New England has identified a number of concerns centering on questions of regional equity. These range from concern over the degree to which coal conversion initiatives addressed to the industrial sector will accelerate the already serious outmigration of industry, issues associated with interregional transport of pollutants from fossil fuel combustion, to issues concerning the imposition of taxes triggered by conservation performance. This type of analysis, therefore, provides a feedback mechanism raising concerns of importance in the implementation of the policy being addressed.

In some cases, constraints are identified which will result in an inability to meet future energy or environmental goals. Such things as shortages of water or class I air quality regions will clearly constrain local development of energy resources.

These and many other factors must be considered in energy planning, and the regional assessments provide the fine structure for such planning.

National assessments, technology assessments, and regional assessments when taken together give those responsible for developing energy and environmental policies the information and analytical base needed in order to come up with plans which can be implemented.

RELATED EPRI PROGRAMS

Ralph M. Perhac

Program Manager, EPRI

INTRODUCTION

The Electric Power Research Institute (EPRI), through its funding activities, seeks to develop a coordinated electric power research program. The Environmental Assessment Department of EPRI is responsible for assessing the environmental effects of electric energy production. Actually, environmental studies are an important part of the work of all of EPRI's technical divisions. In fact, nearly half of EPRI's budget is used for environmentally-related projects. The Environmental Assessment Department, however, is the only EPRI group whose primary function is assessing environmental impacts. In order to fulfill its charge, the Department is organized into three programs: (1) Health Effects and Biomedical Studies, (2) Ecology, and (3) Physical Factors. The 1978 budget for the department is approximately $13 million, with an expected rise to over $25 million in 1981 (Table 1). This increase of nearly 100 percent in three years exceeds that of EPRI as a whole, the EPRI budget rising from about $190 million (1978) to nearly $275 million in 1981, a 45 percent increase. Obviously, concern over environmental consequences plays an important role in EPRI's thinking.

An important emphasis in EPRI's funding is on problems related to the use of fossil fuels (Table 2). Similarly, the focus of the Environmental Assessment is on atmospheric pollution arising from coal-burning plants. The Department's prime concern is with pollution effects on biota, especially on man. The Ecology and Health Effects programs account for nearly two-thirds of the 1978 budget. The Physical Factors Program, however, plays a significant role in that it provides the information on the identification of pollutants, their physico-chemical nature and their fate, i.e., it provides the measurements needed for environmental assessment. The importance of the Program is shown in the budget allocations. The remainder of this paper will deal entirely with the activities of the Physical Factors Program.

PHYSICAL FACTORS PROGRAM

OBJECTIVES

The concern of the Physical Factors Program is with the physical and chemical environmental consequences of electric energy generation. More specifically, the Program's objectives are to define pollutant distribution and the industry's contribution to that distribution. It is the latter aspect (defining the industry contribution) which distinguishes the Program from similar ones in governmental organizations. To achieve its two objectives, the Physical Factors Program is divided into two sub-programs: (1) Identification, Characterization and Monitoring, and (2) Transport and Interaction. Defining pollutant distribution is principally the charge of the first sub-program; defining the industry contribution falls into the second. Like the Environmental Assessment Department as a whole, the Physical Factors Program strongly emphasizes studies related to air pollution and coal burning. Although present emphasis is on air pollution, research is being directed increasingly toward studies of pollutants in terrestrial and aquatic environments and on fuels other than coal.

In developing a research program, attention has been directed to specific pollutants and to some specific, broad environmental problems (Table 3). At present, the emphasis on specific pollutants is on sulfur compounds, nitrogen compounds, trace metals, and organic pollutants (principally polycyclic organics). The broad, environmental problems receiving attention are regional distribution of pollutants, acid precipitation, visibility, and disposal of solid waste. The broad, environmental problems cannot be studied independently; studies of specific pollutants are essential to an understanding of general problems. For example, the program on acid precipitation really has no meaning unless it is coupled to a program of research on atmospheric sulfur species.

IDENTIFICATION, CHARACTERIZATION AND MONITORING

This sub-program involves much more than just identifying and measuring pollutant levels. It comprises three facets: (1) analytical validation, (2) analytical development and improvement, and (3) identification/ measuring. The analytical validation focus is on evaluating existing analytical techniques. One example is a study by Radian Corporation (Austin, Texas) aimed at evaluating the magnitude of error in measuring atmospheric sulfate concentrations with the use of high-volume filters. The specific error suspected was that arising from the possibility that sulfates might actually form (from SO_2) on the filter itself. Such formation would, of course, result in more sulfate being measured than actually exists in the atmosphere. If secondary sulfate formation is significant, then existing data are suspect, and the basis of many health-effects studies would be without a firm foundation. The EPRI-supported research did show, indeed, that SO_2 on standard glass-fiber filters will convert to sulfates in amounts equivalent to 1.6 to 8.9 $\mu g/m^3$. The problem is especially severe for samples collected over short periods of time (2-3 hours). Fortunately, the problem can be minimized by pre-treatment of filters with acid, by using long sampling times, and especially by use of teflon-coated filters.

The sub-program has (and is) supporting a number of projects which deal with developing new analytical techniques. We have put over $400,000 into developing means of identifying specific POM isomers. A project at the University of Tennessee has been successful in using matrix isolation, coupled with fluorescence and infrared spectroscopy, for identification of a number of isomers in simple, synthetic mixtures. Work is continuing, but with natural samples, including coal-conversion liquids. We have also funded SRI International for the development of a truck-mounted lidar unit for measuring atmospheric concentration of SO_2, NO_2, and O_3. Work is about to start on fabricating an airborne lidar for measuring particle distribution. Long-range plans call for ultimately developing a UV-IR unit which can be airplane-mounted and which is capable of analyzing the atmosphere for a wide range of atmospheric gases and particles.

Identification and measurement of pollutants is an important part of the sub-program. We are supporting extensive studies on trace metals and organics in the New York City atmosphere (New York University Institute of Environmental Medicine). This study has already demonstrated that the trace metal contribution to atmospheric pollution from automobiles has doubled since 1969, whereas that from oil burning (homes, industry, and power plants) has halved, now comprising only 11 percent of the total trace metal inventory in the atmosphere. Present work in the project emphasizes organic pollutants and their source attribution. EPRI is also supporting, at the University of Wisconsin-Milwaukee, some very sophisticated (and pioneering) research on speciation of particulate sulfur compounds (phase identification) through the use of such surface techniques as SEM, Auger, ESCA, and SIMS. Perhaps one of the most significant voids in knowledge of the atmospheric chemistry of sulfur is the lack of good data on the chemical form of particulate sulfur compounds. The EPRI-sponsored work at Wisconsin should shed considerable light on the subject and should prove exceedingly valuable for studies of SO_2 oxidation to sulfates and for inhalation toxicology research.

TRANSPORT AND INTERACTIONS

The sub-program on Transport and Interactions is concerned with two things: (1) reaction mechanism and (2) fate of pollutants. Fate studies are essential for assessing biotic impacts. Elucidating reaction mechanisms (and fate studies) is needed for understanding such problems as acid precipitation and for defining the industry contribution to pollution levels. Perhaps the most important project in the Transport and Interactions sub-program is the $6.25 million Sulfate Regional Experiment (the SURE program). SURE's goal is to define the relation between regional, ambient concentrations of a secondary pollutant (e.g., sulfates) and local emissions of its precursor (e.g., SO_2). Such information is vital if an ambient sulfate standard is promulgated. To achieve its goal, SURE involves an extensive monitoring program of air quality at 54 ground stations throughout northeastern United States (Environmental Research & Technology). The project also involves use of airplanes for measuring air quality (Meteorological Research Inc. and Research Triangle Institute) and development of a thorough emissions inventory (GCA Corp.). Coordinating with SURE are plume studies of SO_2 conversion (Battelle Northwest Laboratories), dry deposition (ARAP), and measurement of biogenic emissions of sulfur compounds (Washington State University).

A newly developing focus for the Transport and Interactions sub-program is on acid precipitation. Some work is being supported on measuring acid precipitation (RPI) but research will also be directed toward atmospheric chemistry and the formation of acid droplets in clouds. A new project (Central Electricity Research Laboratory, Great Britain) will attempt to study changes in cloud water chemistry by monitoring the British industrial plume as it interacts with clouds over the North Sea from England to a point of rainfall in Norway. A second, newly developing focus is on visibility degradation. Specifically, we are funding research on means of measuring visibility degradation and on the atmospheric chemistry which causes such degradation.

FUTURE DIRECTION

During the first few years of EPRI's existence (1974-1977), much of the effort in the Physical Factors Program was on identification and characterization of pollutants. Emphasis is now definitely shifting to an understanding of the physico-chemical reactions which occur in the environment and the role of these reactions in a number of broad environmental problems. For example, we are rapidly expanding our efforts in atmospheric reactions of nitrogen oxides, the goal being to use the information to understand better the formation of acid rain. Similarly, our research on the kinetics of SO_2 oxidation feeds into our acid rain and visibility projects.

With regard to specific pollutants, nearly all our effort has been on sulfur compounds. We are now expanding our nitrogen effort and we expect to increase considerably our funding of research on organic pollutants. Our emphasis in studying specific pollutants is on individual species identification and on reaction mechanisms. In the area of broad environmental problems, we already have a sizeable effort in regional distribution studies and we are now expanding our acid precipitation and our visibility programs. In the future, we anticipate considerably more effort on solid waste disposal and possibly on extensive studies of plume model validation.

Many of the projects we support are based on ideas or proposals which we have received from the scientific community. Without the assistance of that community in program planning and in evaluating projects, our achievements would be considerably less than they are. We are indebted to the enthusiastic cooperation shown by our colleagues both in the utility industry and in the scientific community at large.

TABLE 1

Budget - Environmental Assessment Department

($ millions)

Program	1978	1979	1980	1981
Health Effects	4.6	7.3	7.2	9.7
Ecology	3.2	3.0	3.8	3.8
Physical Factors	4.7	4.5	6.8	8.9
EPRI	193	202	232	274

TABLE 2

Budget - EPRI Technical Divisions - 1978

($ millions)

Fossil Fuel & Advanced Systems	Nuclear	Electrical Systems	Energy Analysis & Environment
83.1	53.7	32.8	20.9

Total = 190.5 + 2.50* = 193

* $2.5 million not designated to a specific division

TABLE 3

Programmatic Interests - Physical Factors Program

Sulfur compounds	Nitrogen compounds	Organic compounds	Trace Metals

Environmental Problems

Pollutant Distribution	Visibility	Acid Precipitation	Solid Waste

EPA Air Programs' Use of Environmental Assessments

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Abstract

Under the Environmental Protection Agency's legislative authority, a variety of strategies are available for controlling air pollution. Principal among these are direct emission standards for specific new sources which represent the best demonstrated control technology, direct emission standards for both new and existing sources to minimize specific hazardous pollutants, ambient air quality standards for selected pollutants which are necessary to protect the public health and welfare, mobile source emissions controls and fuel additive standards which assist in protecting the public health and welfare, and programs to prevent significant deterioration of air quality. This presentation describes these various alternative strategies, and discusses how environmental assessments can assist in (1) setting priorities for the pollutants and sources to be controlled, (2) selecting the strategy or combination of strategies to be employed, and (3) assessing the necessary or desired level of control.

Protection of the environment is a very complex process, and environmental assessment has a very important role in that process. Pollution exists in various media—air, water, solid waste, pesticides, etc.—and is controlled through various regulatory programs, either individually or in combination.

For some forms of pollution, the media and the appropriate regulatory programs are obvious. For others, some form of environmental assessment is essential to identify the significant media and the most effective regulatory program or programs. For this purpose, the environment assessment need not identify all the details of the problem—it is normally necessary to identify only the broad aspects of the problem.

In the case of pollutants for which air is identified as the primary or at least a significant medium, the appropriate strategy within the air pollution control program must then be identified. The current air pollution control program consists of two separate but interrelated broad strategies. I will refer to these two broad strategies as "National Emission Standards" and "Air Quality Management," and will explain each separately even though both strategies are mutually supporting.

National Emission Standards

There are four major types of National Emission Standards: (1) Motor Vehicle Emission Standards, (2) New Source Performance Standards, (3) National Emission Standards for Hazardous Pollutants, and (4) Fuel Additive Standards. Each type of National Emission Standard has advantages and disadvantages, and environmental assessments can assist in selecting the appropriate standard.

The Motor Vehicle Emission Standards are essentially legislated by the Congress. They are imposed directly upon the motor vehicle manufacturer, and their primary purpose is to reduce harmful vehicle exhaust to the lowest feasible level in order to assist in managing air quality. In many areas, particularly major cities, the current motor vehicle emission standards are not, by themselves, adequate to protect the public health. In these areas, various forms of air quality management must be implemented to supplement the emission standards.

The New Source Performance Standards are developed by EPA on a national level to ensure that the best demonstrated controls (considering costs) are applied to all major stationary sources of air pollution. New Source Performance Standards represent the maximum emissions that new stationary sources are permitted to emit. A case-by-case determination is also required to determine if additional controls can be applied to either protect the public health and welfare, or to prevent significant deterioration of air quality in clean areas of the country.

The National Emission Standards for Hazardous Pollutants (NESHAPS) are applied to both new and existing stationary sources of very specific pollutants which are particularly hazardous to the public health. NESHAPS are applied to a relatively few pollutants, generally emitted by a relatively few sources, and represent very stringent emission standards which are necessary to solve very severe problems.

The fourth major type of National Emission Standard is the Fuel Additive Standard. Up to this time, EPA has had to restrict fuel additivies of only one pollutant—lead—but it may become necessary to exercise this authority for other pollutants in the future.

National Emission Standards are established by EPA as a national program under which all sources, regardless of location or air quality impact, are treated essentially the same. The strategy of National Emission Standards is very effective in controlling air pollution, but the strategy by itself is not always adequate to protect the public health or welfare, nor to prevent significant deterioration of air quality in clean areas of the country. Hence, in some cases, we employ the second, interrelated, strategy which I will refer to as Air Quality Management.

Air Quality Management

The Air Quality Management Strategy also has four major facets: (1) Primary National Ambient Air Quality Standards, (2) Secondary National Ambient Air Quality Standards, (3) Prevention of Significant Deterioration of Air Quality, and (4) Enhancement of Visibility. Air Quality Management basically consists of defining a maximum acceptable level of pollution in the ambient air, and then controlling both the emissions from sources and the location of sources to ensure that the acceptable level of pollution is not exceeded.

Primary National Ambient Air Quality Standards are established to protect the public health. They are based upon the concept that there is a threshold level of pollution below which the public health is not jeopardized. That level is identified from health effect studies, and the primary standard is then established with an adequate margin of safety. The original primary standards were to have been attained by mid-1975 in most areas. Although we made substantial progress toward attainment, many areas still have air quality worse than the primary standards. The Clean Air Act of 1977 now requires attainment by 1982 with, in some cases, the possibility of extensions to 1987.

Secondary National Ambient Air Quality Standards are established to protect the public welfare. They are based upon the same threshold concept as primary standards, but the effect being protected against is welfare related such as materials damage, soiling, crop damage, etc. Although for some pollutants the primary and secondary standards are identical, secondary standards are generally more stringent than primary standards. Also, whereas primary standards are to be attained by a specific date, secondary standards have no statutory deadline for attainment so long as they are attained within a "reasonable" time.

Prevention of Significant Deterioration is the third major Air Quality Management program. It was established to protect the relatively clean areas of the country from becoming dirtier. Unlike the ambient standards which are based upon a threshold concept, significant deterioration is based upon an incremental deterioration above some pre-existing level of air quality.

What constitutes "significant" deterioration, however, may be different in some areas of the country than in other areas. Therefore, the local people may classify their areas into one of three classes. A Class I area is intended to have virtually no deterioration. A Class II area (which is the most common classification) may permit moderate deterioration without that deterioration being "significant." The Class III classification is reserved for areas in which air quality may not deteriorate to the level of the the health or welfare related ambient standards. At this time, no areas have been classified as Class III.

The fourth major Air Quality Management program is brand new. It was established by the Clean Air Act of 1977 and is intended to protect and enhance visibility. This program is still a year and a half from initial implementation, because much research and regulatory development work must still be done. It will probably not have much impact in the heavily industrialized areas of the nation, but I anticipate a significant impact on the large isolated sources of air pollution in the West.

Summary

As you can see, the air pollution control program is very complicated. It has two basic strategies—National Emission Standards and Air Quality Management. Each of these strategies has four basic components providing a total of eight major regulatory options through which, either individually or in combination, air pollution can be controlled.

The choice of options can be difficult, yet making the correct choice is essential to the success of the air program. The other environmental programs—water, solid waste, radiation, toxic substances, etc.—also have a variety of options available for achieving their goals. From my perspective, the main benefit (although by no means the only benefit) of environmental assessment is to assist in determining and prioritizing the goals, selecting the appropriate regulatory program or programs, and then selecting from the various options the most effective methods for achieving the goals.

This is a very important task. When we speak of environmental programs we are speaking of billions of dollars annually, and we are speaking of the health, welfare, and quality of life of everyone in the nation. I encourage you in your endeavors during this symposium, and I wish you great success.

AN INTEGRATED APPROACH TO ASSESSMENT AND CONTROL OF INDUSTRIAL POLLUTION PROBLEMS

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Abstract

EPA now has comprehensive legislative and court mandates for regulating all pollution resulting from the production and use of industrial chemicals and products. Emphasis is being placed on toxic and hazardous pollutants. To aid EPA in focusing its attention and future efforts on those pollution problems which have the greatest health and ecological impacts, EPA has developed in one organizational unit an approach for assessing simultaneously the environmental impacts of industrial pollution discharged to the air, water, land and municipal systems. This multimedia approach necessarily involves the active participation of the appropriate EPA regulatory components and industry. Field sampling and RD&D programs are initiated based upon the outcome of the integrated industrial assessment approach.

Introduction

In the last several years, there has been a major change in emphasis in the Agency's environmental pollution control programs. This has resulted principally from recent legislative and court mandates. This change began with the signing of the Resource Conservation and Recovery Act of 1976 (PL 94-580) and the Toxic Substances Control Act also of 1976 (PL 94-461). These legislative Acts, along with the Clean Air Act Amendments of 1970 (PL 91-604) and the Water Pollution Control Act Amendments of 1972 (PL 95-500), provided EPA with comprehensive legislation to address all aspects (i.e., air, water, land and exposure through consumer products) of environmental pollution. In addition to this comprehensive legislation, there has been, in the last two years, increased emphasis on specific toxic and hazardous pollutants. This, of course, has been brought about by the signing of TSCA and, more immediately impacting, the court settlement in 1976 between EPA and the National Resources Defense Council (NRDC) requiring EPA to develop effluent guidelines for 65 pollutant categories suspected of toxic and hazardous properties which may be discharged from 21 industry categories over the next three years. In addition to these mandates, the Clean Air Act Amendments of 1977 also placed more emphasis on specific hazardous pollutants such as arsenic, lead, cadmium, polycyclic organic materials and required an increased rate of regulation for the conventional criteria pollutants. The Clean Water Act Amendments of 1977 supported the specific pollutant emphasis and the requirements of the NRDC/EPA Consent Decree of 1976. The net result was to place greater emphasis on industrial sources of pollution and the specific processes which generate known or potentially hazardous and toxic pollutants, regardless of whether they pollute the air, water, land, or are discharged to municipal systems.

Previous activities within the Agency have focused on generic or surrogate pollutant control of the criteria pollutants, NO_x, SO_x total particulate, total hydrocarbons and, similarly, BOD, COD, pH, suspended solids. Little or no data base has been developed by EPA or its precedessor agencies on the characterization and control of industrial discharges considering specific pollutants or chemicals thought to be toxic or hazardous. Consequently, to meet the mandates of the recent legislation and court settlements, EPA's regulatory and R&D offices have initiated extensive national efforts to define and assess the industrial pollution problems created by specific toxic and hazardous pollutants. These efforts by EPA's regulatory offices have been undertaken using the traditional approaches, that is, along single media lines with the appropriate air, water, and solid waste office addressing its own limited portion of the total industrial problem. As a result of an organizational change in EPA's Office of Research and Development in 1975, research's approach to addressing industrial pollution problems deviated from this conventional approach.

In 1975, the reorganization of the Office of Research and Development resulted in the formation of two laboratories, the Industrial Environmental Research Laboratory in Cincinnati, Ohio, and the Industrial Environmental Research Laboratory in Research Triangle Park, North Carolina. These laboratories were provided unique charters to address industrial pollution problems. Specifically, they were charged with the responsibility to assess and to develop control methods for the total gaseous, liquid, and solid waste pollution problems of industry. This represented the premiere, within the Agency, of two organizational units with the responsibility to address the total industrial pollution problem and to place their emphasis on an integrated or "multimedia" solution to the air, water, and solid wastes pollution problems of industry. To respond to this unique and broad responsibility, it was necessary for these laboratories to develop systematic and comprehensive approaches for examining industries, their processes and practices, and concomitant pollution problems.

This paper is a brief description of the approach which evolved at the industrial laboratory in Cincinnati from consideration of the multimedia pollution problems of the nonferrous metals production and inorganic and organic chemicals industries. A specific discussion of the nonferrous metals assessment activities is scheduled for later in the program. Consequently, this presentation will be limited principally to the general approach which has been entitled "An Integrated Multimedia Approach to Assessment and Control of Industrial Pollution Problems."

*Speaker

The Multimedia Approach to Environmental Assessments - An Overview

The multimedia approach was developed to assure full utilization of available information sources, principally the open literature, government reports, and other information generated in the Government's enforcement and regulatory activities. It relies heavily upon site visits and the use of nongovernment expertise including consultants and industrial technologists. Field sampling and analysis of industrial process waste streams is not a part of the initial industrial assessment. Rather, the results of the assessment provide a comprehensive and scientific basis upon which appropriate research and development and field sampling and analysis programs can be planned and implemented.

Goals of the Assessment

The following are major products or results desired through implementation of the "multimedia" approach: (1) to identify the most serious industrial pollution problems based upon potential health and ecological impacts regardless of the type of discharge, i.e., to the air, water, land, or municipal systems; (2) to help the Agency concentrate its limited resources, particularly in the future, on the more serious industrial pollution problems; (3) to establish an EPA understanding, from a pollution control perspective, of industrial processes, operations, and practices to facilitate the development and implementation by industry of pollution control methods; (4) to establish government-industry working relationships to solve these industrial pollution problems through technological applications; (5) to develop pollution control technologies that minimize secondary pollution effects, that is, avoid transfer of the pollution problem to another media, and finally (6) to provide a basis upon which a more efficient and scientific approach can be taken to developing experimental data on the characterization and control of industrial pollution problems for (a) regulatory purposes or (b) for better definition of pollution problems and their control.

Products of the Environmental Assessment

The initial multimedia industry assessment results in three major products: (1) a preliminary data base on the industry including companies involved, production sites, products, processes, discharges, pollution control technologies, associated health effects; (2) the verified data base, derived from a detailed analysis and extensive expert review supported by site visits of the preliminary data base; and (3) the initial assessment report identifying the most serious industrial pollution problems that can be established from the available literature and the major information gaps that exist in defining the total industrial pollution problems.

Development of a Preliminary Data Base

The development of a preliminary data base is composed of four major tasks, shown in Figure 1. These are (1) the definition of the industry, (2) identification of the processes and associated discharges to the environment, (3) the assembling of available health and ecological effects data associated with the industry, its discharges or components of the discharges, and (4) a review of the preliminary data base by industry and health and ecological effects experts. The overall purpose of this initial effort is to be complete and comprehensive in obtaining, from the open literature and other available sources, all information that relates to the specific industrial products, processes, and associated pollution problems. The first three of these tasks are often conducted simultaneously.

Industry Definition

The industry definition task establishes the identity of an industrial category, linking together competitive companies producing similar products. The approach attempts to consider actual industrial conditions and operations. Information is assembled, however, in such a way that it can be cross-referenced to standard industrial classification codes (SIC) for use in conjunction with economic analyses and related to the Agency's regulatory and enforcement activities. Key factors in defining an industry include the companies involved, raw materials consumed, products and their uses, overall process flow sheets, capacities and actual production, trends and forecasts with emphasis on growth, new production processes, economic status, and environmental impacts of the overall operations.

These basic factors are analyzed and developed so as to emphasize their relationship to environmental control and to facilitate assessment of the economic impact of potential regulations. For example, analyses of raw materials and processes provide information that can aid in determining the effects changing feedstock composition and processing conditions may have on environmental pollution. A complete product list is particularly useful in that it defines a limitation on the boundaries of an industry, its technologies and the related environmental impacts. These lists, developed during the industry definition phase, lead to a family of processes by which the product materials can be made. Information concerning industrial trends is also helpful especially when the use of alternative feedstocks may alter the environmental impact of an industry's discharges.

Identification of Processes and Discharges

Process flow sheets depicting the industry as a series of interrelated modules is an important tool. It is used to interrelate all process operations from raw materials, including their production for integrated industrial operations, to the final production of goods and to indicate all discharges to the air, water, land, or municipal systems. Each production process is described in the following terms:

Function of each unit operation
Feed materials
Operating conditions
Utility requirements
Waste streams
Pollution control technologies
Occupational and environmental
  health effects
Reference materials
Related SIC codes

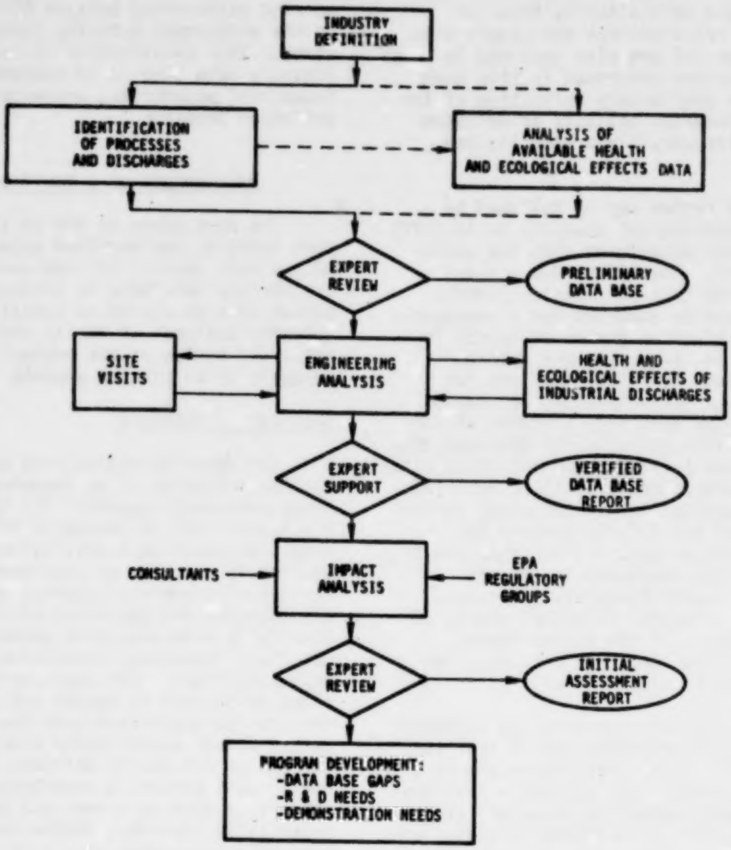
INDUSTRY DEFINITION
IDENTIFICATION OF PROCESSES AND DISCHARGES
ANALYSIS OF AVAILABLE HEALTH AND ECOLOGICAL EFFECTS DATA
EXPERT REVIEW
PRELIMINARY DATA BASE
SITE VISITS
ENGINEERING ANALYSIS
HEALTH AND ECOLOGICAL EFFECTS OF INDUSTRIAL DISCHARGES
EXPERT SUPPORT
VERIFIED DATA BASE REPORT
CONSULTANTS
IMPACT ANALYSIS
EPA REGULATORY GROUPS
EXPERT REVIEW
INITIAL ASSESSMENT REPORT
PROGRAM DEVELOPMENT:
-DATA BASE GAPS
-R & D NEEDS
-DEMONSTRATION NEEDS

Figure 1. Industry Assessment and Program Development Protocol

This task identifies potentially hazardous discharges warranting detailed study and puts the industry's multimedia or total pollution problems into the proper perspective. When data are nonexistent or limited to conventional pollutants, preliminary estimation of specific pollutants can be made through limited engineering analysis. Studies by industry, EPA, Department of Interior, Department of Commerce, and the Department of Energy can provide much of the data on important processes. Trade journals, Department of Commerce patents, key word literature searches, and standard reference works such as the Encyclopedia of Chemical Technology (Kirk Othmer), Chemical Process Industries (Shreve) and Textbook of Industrial Chemistry (Riegel) are used to obtain information on lesser known processes. It is also important in this step to make a preliminary evaluation of foreign process and control technologies under development or in actual use. Such information is useful in assessing trends and potentially significant process changes.

Review of Available Health and Ecological Effects Data

Assembling existing mortality/morbidity data is done principally to aid in establishing the priorities for industrial processes or discharges requiring further work. Consideration of the ratio of death to population (regardless of cause) and relative incidence of disease is made with the intent of identifying correlations between specific industrial activities or processes and health effects. This is conducted in cases where information is available and the proliferation of plant sites does not prevent the isolation of the effects of the plant or process in question. Toxicity data on materials, additives, products and emissions from production processes are searched through computerized data bases such as the National Library of Medicines (NLM), Toxline and Medline and related National Institute of Occupational Safety and Health and EPA health files. Any industry-associated compounds known or suspected to be carcinogenic, teratogenic, or mutagenic are given special attention. Substances known to have high potential for producing chronic toxicity are also included. Industry-associated compounds appearing on other lists of toxic substances such as those maintained by NIOSH or structure activity relationships that imply significant toxic potential are also included in this survey. The information generated in this task can also serve as a preliminary definition of the scope of required chemical analysis of emission streams in future industry field sampling and analysis programs.

The literature review may be followed by a retrospective epidemiological analysis to identify actual health impacts associated with the operations of an industry. The literature reviews serve to indicate the type of disease-specific mortality that should be examined for a representative number of production processes in the industry. Using Health, Education and Welfare Department (HEW) data, mortality profiles for counties exposed to a given industry discharges can be compared to the mortality profiles of surrounding counties. The selection of diseases used in mortality profiles is based upon available data concerning known target organs of toxic materials. Plants must have operated for a sufficient period of time to allow for the latency periods for chronic diseases such as cancer. The most specific mortality data are available in the HEW publication, "U.S. Cancer Mortality by County, 1953 through 1969." Another principal source of data, "Vital Statistics of the United States, 1971, Volume II - Mortality," has the advantage of not being limited to cancer mortality.

Although this type of retrospective epidemiological analysis is an extremely useful tool for establishing priorities and identifying the most potentially serious industrial pollution problems, it cannot conclusively establish cause and effect relationships. However, occupational diseases are often found to be an early warning of related environmental health problems which may not surface until many years later. On the other hand, the difficulty in separating health effects directly related to industrial pollution from general urban pollution will often preclude any utilization of this type of analysis. These studies simply serve as a mechanism for focusing the emphasis on suspected problem areas and for identifying where field epidemiological studies may become a necessary part of a recommended research program in the future.

Data collected in the first three tasks are assembled in a format, which allows convenient and consistent display of pertinent process and discharge data for individual and comparative review and analysis. One convenient format is that used in the EPA publication entitled, "Industrial Profiles for Environmental Use" (EPA-600/2-77-023). The assembled information is then submitted for review by industry and health experts to insure that no significant omissions of processes, discharges, or related health and ecological data have been made and that the industry is correctly defined. Upon completion of the review, the preliminary industrial data base is considered complete. The importance of this phase and the need for completeness in assembling available information is stressed as all future work is dependent upon the validity and completeness of the preliminary data base.

The importance of building and encouraging a working partnership between EPA and industry early in the assessment activity cannot be overemphasized. This relationship is essential if the preliminary data base is to represent real world industrial boundaries, processes, practices and pollution problems.

Development of a Verified Data Base

The next phase in the initial industry assessment leads to the verified data base and consists of two main tasks: (1) engineering analysis of the preliminary data base on production processes supported by site visits to specific plants and more directed analysis of health and ecological effects data; (2) review of the product of the engineering analysis by practicing experts in the industry.

Engineering Analysis

The detailed engineering analysis of the production processes of an industry is performed for three principal reasons: (1) to identify obscure discharges; (2) to determine if closer attention should be given to a unit operation traditionally ignored in the past or considered only to have limited environmental impact; and (3) to predict the quantity and character of the discharges associated with each unit operation based upon materials processed, production capacity and process conditions. The engineering analysis can often be focused by health and ecological data that can be associated with the production products, plants and/or their processes. When process discharges are poorly defined, however, and little health data exists, a step-by-step analysis of the process is done to ferret out unidentified but potentially hazardous discharges. This analysis must be supplemented with site visits by qualified personnel to fill gaps in process descriptions and to gather data on operating conditions and factors that affect pollutant discharges.

Expert Review

The results from the engineering analysis and the expert review provide a verified data base upon which the air, water and solid waste pollution problems can be assessed to identify those that are the most serious. In addition, the data base is structured in such a way that it can now provide a site specific basis upon which industrial processes and operations can be examined comprehensively and scientifically. It can now provide the basis upon which field sampling and analysis programs can be designed to generate technically sound data suitable for developing regulations and control technology programs. The verified data base is assembled in a manner that is conveniently handled manually or stored for computer manipulation but in either case can be updated continuously. The need for computer applications is based primarily on the complexity of the industry.

Preparation of an Initial Assessment Report

Impact Analysis

The final step before development of appropriate R&D and field sampling and analysis programs is the impact analysis or assessment of the total environmental pollution problems created by an industry's discharges to the air, water, land or municipal systems. This analysis is principally an in-house EPA effort involving the active participation and support of EPA health, ecological, technology, regulatory and enforcement personnel. The purpose of the impact analysis is to determine the most serious public health hazards caused by industrial pollution considering proximity of the discharge sources to population centers, transport of pollutants, health hazards presented by the pollutants versus the available control technologies. Commercial and prototype control technologies are examined for their technical and economical feasibility to control both conventional and specific hazardous pollutant discharges. Particular emphasis is directed toward insuring that pollution problems are not transferred from one media to another. Consequently, ultimate disposal of collected wastes with hazardous properties is given priority consideration. Priority is also given to control of those processes and discharges for which hazardous properties are conclusively identified or strongly suspected. Experience indicates that this initial industry assessment will normally identify those control technologies that have been applied to many waste streams before their effectiveness to control specific pollutants has been demonstrated. Quantitative characterization of many waste streams will also be limited to surrogate pollutants. Because of such data gaps, the initial assessment can be expected to identify more unknowns regarding sources of particularly harmful pollutants and the applicability of control methods than demonstrated solutions to problems. In spite of this limitation, however, it provides a comprehensive data base for identifying the most serious industrial pollution sources upon which future field sampling and analysis and RD&D programs can be focused.

Critical Expert Review

Before the assessment results are used in guiding future program development activities, the results of the impact analysis are subjected to a final, highly critical review. Reviewers include representatives of the industry, related industry associations, EPA's regulatory and enforcement offices, EPA research and health effects laboratories, consulting engineers, public health organizations, and universities. The purpose of this review is to insure that the program development activities to follow are based upon an accurate and complete a basis as possible.

Resources Required for Environmental Asessments

The resources required for conducting an initial industry assessment are shown in Figure 2 and normally range from 500 to 2,000 professional manhours, depending upon the number, complexity and obscurity of the processes used by the industry. This range is based upon experience to data which has shown that approximately 20-50 professional manhours are required to examine a single production process. The major expenses are associated with the engineering and retrospective epidemiological analyses and development of individual process descriptions. Typically, initial industry assessments conducted to date have been completed in six months to one year.

Applications of the Integrated Approach

The initial industry assessment and verified data base are just the beginning of the efforts necessary to define and control industrial pollution problems. However, they can form a basis upon which research and regulatory programs can be coordinated, planned, and implemented to address the total industrial pollution problem. While the "multimedia" approach has been applied only to research activities to date, there has been some utilization for structuring and coordinating related research and regulatory sampling and analysis programs. Specifically, the verified data base for the industrial organic chemicals industry, termed the Organic Chemical Producers Data Base (OCPDB) has been used to develop field sampling programs for both air and water regulations development for this industry. The OCPDB was used to identify where specific products and processes to be regulated were employed and to specify the minimum number of production sites necessary to be sampled to cover all combinations of products and processes. The computerized data base also provided alternative locations should the original sites not be convenient for sampling.

The multimedia assessment approach and the same Organic Chemical Producers Data Base are also being used to structure a proposed program to support EPA's Office of Toxic Substances in determining the total human exposure potential, through process discharges and direct contact from the production and downstream use, of the major 400 U.S. industrial organic chemicals. In addition, the approach will be used to assess the electronics and mechanical products industries. Based upon the data bases derived from the integrated assessment of these highly complex and diverse industries, a statistically sound field sampling and analysis program will be developed and implemented. The results of this effort will provide the technical basis for establishing pretreatment and effluent guidelines for the most serious sources of the 65 pollutant categories defined in the 1976 NRDC Consent Decree.

All of these programs will be used to validate and refine the integrated assessment approach. If successful, it could provide guidelines upon which the data necessary for research purposes and for air, water, solid waste, and toxic substances regulations can be obtained simultaneously in cooperative EPA field sampling and analysis programs. An ongoing study supporting this concept is an attempt to identify all of the Agency's known data requirements for assessing and regulating industrial pollution discharges. The purpose is to establish a compendium of all common industrial and process waste stream data required for each activity.

Conclusions

These efforts represent but a few of those ongoing which utilize the integrated approach to assessing industrial pollution problems. The results will determine to a large extent the acceptance and general utility of this approach by the Agency in its future activities to develop

Activity	Total Professional Manhours	Professional Skill Required
Industry Definition and Identification of Industrial Processes	10%	Jr. engineering personnel under supervision of Sr. staff, chemical engineers
Review of Health and Ecological Effects Data	10%	Industrial hygienists, toxicologists, biostatisticians
Development of Process Descriptions	20%	Jr. engineering personnel under supervision of Sr. staff, chemical engineers
Engineering Analysis and Retrospective Epidemiological Analysis	25%	Experienced chemical engineers, industrial hygienists, toxicologists, biostatisticians
Project Management	15%	Sr. engineering staff
Definition of Data Needs, Preliminary Definition of R&D Needs, Report Preparation	20%	Engineering staff

Figure 2. Description of Personnel Needs During Industrial Environmental Assessments

a data base on specific toxic and hazardous pollutants produced by industrial processes. The Agency has already initiated major data gathering efforts along traditional media lines. We hope that the multimedia approach will provide a vehicle by which this information can be gathered more efficiently with a minimum impact on industry and will result in technology and regulations that address the most serious industrial pollution problems.

SOURCE ASSESSMENT METHODOLOGY

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Abstract. The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the goals of environmental legislation. IERL performs Source Assessments for determining the need to reduce emissions and discharges from pollution sources. This paper presents a discussion of the steps involved in preparing a Source Assessment, decisionmaking information used by IERL and an example of the effect of data uncertainty on IERL decisionmaking.

Introduction

The objective of a Source Assessment is to provide IERL with sufficient information to determine the need to reduce pollution from stationary sources. A source is an entire industrial, commercial, or municipal operation which is national in scope. An assessment is the determination and extent of pollution based on all available process emissions, discharges and pollution control information. The product of a Source Assessment is a Source Assessment Document (SAD). The result is an EPA decision regarding the need to reduce pollution.

In the following discussion, there will be two items addressed. These are: 1) activities involved in preparing the Source Assessment Document; and 2) information which EPA uses as an aid in determining the need to reduce pollution. To give an overview, expert information from scientists (analytical chemists, sampling personnel, health and ecological experts, meteorologists, etc.) and engineers (chemical, civil, environmental, etc.) is used to prepare a complete assessment of a source. The IERL uses this information in making environmental decisions.

Preparation of a Source Assessment Document

Figure 1 is a diagram of the steps involved in preparing a Source Assessment Document.

Work Plan

A work plan is prepared at the start of each Source Assessment. The objectives of the work plan are two-fold: 1) to describe the proposed study; and 2) to provide IERL with a management control point. The work plan contains the objective and scope of the assessment, technical approach, source definition, benefits expected, timing, anticipated problems and proposed solutions, estimated cost, manpower and performance, project schedule and milestones.

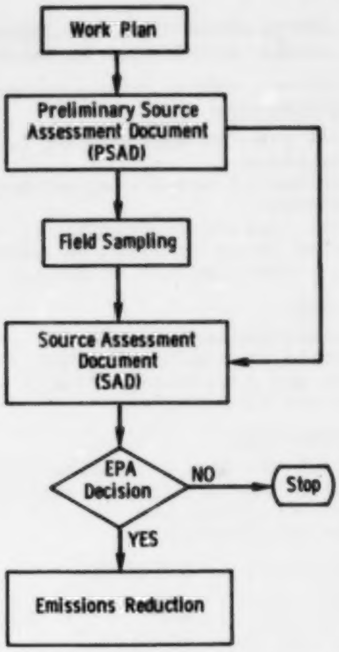
Work Plan
Preliminary Source Assessment Document (PSAD)
Field Sampling
Source Assessment Document (SAD)
EPA Decision
NO
Stop
YES
Emissions Reduction

Figure 1. Steps in performing a Source Assessment.

Preliminary Source Assessment Document (PSAD)

Preparation of the Preliminary Source Assessment Document (PSAD) is initiated upon EPA approval of the work plan. The Preliminary Source Assessment Document looks exactly like the Source Assessment Document. The PSAD is a baseline of information about a source. It is prepared by using available process, emissions, discharges, pollution control and other industry information. It is prepared without extensive field sampling; a presurvey sample is collected and analyzed using methods resembling the Level I Environmental Assessment procedures. The purpose of the presurvey sampling is to identify the types and quantities of previously unknown hazardous or potentially toxic pollutants.

The PSAD is a unique document in contract research efforts. The purpose of the PSAD is to determine if there is sufficient information for IERL decisionmaking. This purpose is expanded as follows: 1) to provide an IERL management control point for development of the SAD; 2) to provide a basis for determining the need to acquire additional information through sampling; 3) to identify the types and quantities of previously unknown hazardous or potentially toxic emissions; and 4) to provide a basis for obtaining additional information from industry.

The PSAD contains the types of information given in Table 1.

TABLE 1. INFORMATION IN A PRELIMINARY SOURCE ASSESSMENT DOCUMENT

Process information

- General process and product flow schematics
- Variations of operations within the industry
- General operating parameters, especially those relating to pollution
- Plant capacities and locations

Pollutant data

- Emission/discharge points
- Materials emitted/discharged
- Health and ecological effects
- Pollutant inventories

Control technology

- State-of-the-Art in control technology
- Extent of application of controls
- Control efficiencies
- Future considerations

Growth and nature of industry

- Process technologies
- Product market areas
- Production rate trends

Reference material

The PSAD is based on information from available information sources. These sources include personnel, published literature, local, state and Federal EPA offices and files, industry surveys, trade associations, presurvey testing at plants, and equipment vendors.

If EPA determines that the PSAD contains sufficient information for decisionmaking purposes, the PSAD is published as a Source Assessment Document. If it does not, a field sampling program is performed to collect the needed, but missing, information.

Field Sampling

A sampling plan is prepared to obtain the information needed for IERL decisionmaking but which is not available in the PSAD. The sampling plan is designed: 1) to allow IERL to exercise options on a cost/effective basis; 2) to provide the protocol for obtaining missing information needed for the Source Assessment Document; and 3) to allow IERL to judge the reliability and acceptability of the sampling and analysis methodology.

It contains a discussion of the additional data required, test site(s) preparations required, sampling and analysis methods, uncertainties and potential problems, and options for test schedules and levels of effort. The sampling and analysis procedures used in the sampling program resemble those of the Level II Environmental Assessment protocols.

Source Assessment Document (SAD)

The product from a source assessment is a Source Assessment Document and it can be prepared with or without field sampling. The SAD contains the same types of information as the PSAD (Table 1). It contains a summary of the study (a concise presentation of all relevant information for IERL to determine the need to reduce pollution); a discussion of the industry, the severity of the pollution from the industry, summary of existing and anticipated control technology, industry trends, unusual results, and supporting data. Each Source Assessment Document must be capable of withstanding scrutiny, credible, factual, accurate, self supporting, complete, concise and lucid.

IERL Decisionmaking Procedures

IERL uses the Source Assessment Document to determine the need to reduce pollution. When it comes to pollution from a source, EPA has only two choices: 1) to do something about the pollution, or 2) to do nothing.

IERL uses a set of criteria as an aid in determining the need to reduce pollution. These criteria are shown in Table 2.

TABLE 2. IERL EVALUATION CRITERIA

Major Criteria

Source severity
Nation emissions burden
State's emissions burdens

Minor Criteria

Affected population
Pollution growth trends

The major criteria are used to determine the need to reduce pollution. The minor criteria are used to modify or prioritize the decision. A description of each of the criteria follows.

Source Severity(s)

Source Severity is defined as the ratio of the concentration to which the population is exposed to the concentration which represents a potentially hazardous concentration.

The following discussion regarding the criteria will be limited to air emissions for simplicity. The same concepts and approaches apply for other pollutant media.

The exposure concentration is the time-averaged maximum ground level concentration as determined by Gaussian plume dispersion methodology. This determination requires expert input from engineers, sampling personnel, analytical chemists and meteorologists.

The potentially hazardous concentration is estimated in two ways. It is the Primary Ambient Air Quality Standard for criteria pollutants. It is a surrogate Primary Ambient Air Quality Standard for noncriteria pollutants. The potentially hazardous concentration requires expert input from health effects personnel.

The values of Source Severity which IERL uses for decisionmaking are shown in Table 3. There are only two decisions to be made: 1) IERL will reduce pollution, or 2) IERL will not reduce pollution.

TABLE 3. SOURCE SEVERITY MEASURE/DECISION

Measure	Decision
$S \equiv \frac{C}{F} \geq 0.05$	There is sufficient cause to reduce pollution.
$S \equiv C < 0.05$	There is not sufficient cause to reduce pollution

The value of $S = 0.05$ as the cut-point was obtained by evaluating the uncertainties involved in engineering data, sampling and analysis results, atmospheric dispersion models, and health effects data. The details of how this cut-point was developed is described in a report entitled: "Source Assessment: Analysis of Uncertainty" (1).

Nation Emissions Burden (B_N)

The National Emissions Burden is the mass of criteria pollutant emissions from a source divided by the national mass of criteria pollutant emissions. This criterion uses engineering and emissions input for a source to develop an emissions inventory for the source. The values which IERL uses for decisionmaking are shown in Table 4. In short, if emissions from a source amount to more than 0.1% of the U.S. total criteria pollutant emissions, then a source is considered as a candidate for emissions reduction.

TABLE 4. NATIONAL EMISSIONS BURDEN[a]

Measure	Decision
$B_N \equiv \frac{\Sigma M_P}{\Sigma M_N} \times 100 \geq 0.1$	There is sufficient cause to reduce emissions
$B_N \equiv \frac{\Sigma M_P}{\Sigma M_N} \times 100 < 0.1$	There is insufficient cause to reduce emissions

[a] Calculated for each criteria pollutant, i.e., Particulates, Sulfur Dioxide, Nitrogen Dioxide Carbon Monoxide, and Hydrocarbons.

State's Emissions Burden (B_S)

The State's Emissions Burden is identical in concept to the National Emissions Burden. It differs only in that it is calculated for each of the 50 states instead of the nation. Table 5 shows that if the State's Emission Burden exceeds 1% of the state's total criteria pollutant emissions, then it is considered as a candidate for emissions reduction.

TABLE 5. STATE'S EMISSIONS BURDENS (B_S)

Measure	Decision
$B_S \equiv \frac{\Sigma M_P}{\Sigma M_S} \times 100 \geq 1$	There is sufficient cause to reduce emissions
$B_S \equiv \frac{\Sigma M_P}{\Sigma M_S} \times 100 < 1$	There is insufficient cause to reduce emissions

Affected Population

The Affected Population is the number of persons exposed to a potentially hazardous environment. It is the number of persons exposed to a Source Severity greater than 1.0. The affected population is not used to determine the need to reduce emissions. It is used in establishing a priority on those sources which require emissions reduction.

Emissions Growth Trends

The emissions growth trends is a measure of predicted future emission rates relative to current emission rates. If a source will go out of business within 5 years, then IERL will not attempt to reduce emissions as this will happen anyway. If a source will significantly reduce its emissions as a result of local or state EPA regulations, then IERL may not consider additional emissions reduction.

IERL Decisionmaking Overview

IERL uses a Source Assessment Document to determine the need to reduce pollution using criteria discussed above. A Source Assessment Document incorporates expert information from engineers, sampling personnel, analytical chemists, meteorologists, and health effects personnel. IERL has a few concerns about the correctness of its decisions. These concerns are:

(1) Is the decision correct?

(2) What impact does data quality have on the correctness of the decision?

(3) Which information areas have the greatest impact on correct decisions?

(4) What can be done to improve the decisionmaking process?

Whether or not any given decision is correct cannot be determined at the time the decision is made. All that can be done at the time the decision is made is to assess the likelihood that the decision is correct. This likelihood is based on the quality of the information on hand at the time the decision is made.

The impact of poor data quality on decisionmaking is that it forces the decision maker to be conservative. This conservation is used to make up for the increased likelihood of incorrect decisions due to poor data quality. An example of how this applies is in the cut-point for Source Severity.

Ideally, IERL would like to base its decisions on a true value of source severity. If a true value of Source Severity could be obtained, IERL's decisionmaking would be based on a cut-point of 1.0. However, the true value of Source Severity is unknown. It can only be estimated. Monsanto Research Corporation's project on the Analysis of Uncertainty showed that the calculated value of Source Severity is within a factor of 20 of the true value of Source Severity. This range of possible true values of Source Severity for a calculated value requires that the IERL cut-point be 0.05 (1/20).

This range of uncertainty in Source Severity is caused by the uncertainties in the data used to calculate Source Severity. These data inputs are:

(1) Emissions data

(2) Dispersion models

(3) Health effects data

The contribution to the total uncertainty is shown in Table 6.

TABLE 6. CONTRIBUTIONS TO UNCERTAINTY IN SOURCE SEVERITY VALUES (1)

Complete reduction of uncertainty here	Yields	Corresponding reduction of uncertainty in source severity
Sampling and analysis	⟶	35%
Health effects data	⟶	80%
Dispersion modeling	⟶	90%

The values shown in Table 6 do not add to 100% because the contributions to total uncertainty for each input are not linear. If the uncertainty in all three areas were completely removed, the uncertainties in Source Severity would be completely removed. Another way of viewing the effect of the uncertainty in each input area is to determine the cut-point which would be used in the decisionmaking process. This is shown in Table 7.

Table 7 shows that as the data quality improves, the degree of conservatism in decisionmaking decreases.

TABLE 7. EFFECT OF UNCERTAINTY REDUCTION ON CUT-POINT FOR SOURCE SEVERITY

Complete reduction of uncertainty here	Yields	Corresponding cut-point for source severity
Sampling and analysis	⟶	0.08
Health effects data	⟶	0.25
Dispersion modeling	⟶	0.5

The specific contributors to Source Severity uncertainty are shown in Table 8. This list of the elements of uncertainty can be used to prioritize the data quality improvement for Source Assessment.

TABLE 8. ELEMENTS OF UNCERTAINTY IN SOURCE SEVERITY

Element of uncertainty	Reduction in total uncertainty if uncertainty in element is eliminated, %	
• Sampling and analysis	35	
Random uncertainty		2
Bias		33
• Dispersion model	90	
Dispersion equation		65[a]
Plume rise		74[a]
• Potentially hazardous concentration	80	
Primary Ambient Air Quality Standards		0
Safety factor on health effects data		80

[a] Uncertainties not linear.

The simplest area to reduce the uncertainty in Source Severity is in the plume rise calculation in the dispersion model. The dispersion model, as currently used in Source Severity, ignores plume rise. Recent EPA studies have shown that the Brigg's equation for plume rise yields a better correlation of predicted versus actual downwind concentrations. Use of the Brigg's equations for plume rise in the dispersion model would reduce source severity uncertainty by 74% or increase the cut-point from 0.05 to 0.19. This is quite simple to do since it only requires a computational change.

The most difficult area to reduce the uncertainty in Source Severity is in the estimation of the potentially hazardous concentration. This concentration requires a great deal of laboratory experimentation to generate the needed health and ecological effects data. Once these data are generated, a value judgement is required to estimate a "safe" or "acceptable" concentration of exposure.

The area where a reduction in data uncertainty has the least impact in reducing Source Severity uncertainty is sampling and analysis. This statement applies when the quality assurance procedures specified by the IERL-RTP Data Quality Manual are followed. Any deviation from those procedures or the procedures specified by the Quality Assurance Branch will increase the uncertainty in sampling and analysis data; hence, Source Severity.

Example

An example is given below to illustrate the results of a rather complex statistical treatment of data used in Source Assessment. Emissions from the main process vent at carbon black plants are used in the example. Table 9 shows the materials emitted as determined through field sampling. The Source Severities for carbon monoxide, particulates and hydrogen sulfide will be used.

TABLE 9. CARBON BLACK EMISSION FACTORS[a]

Material emitted	Emission factor, g/kg product
Criteria pollutants	
Particulates[b]	0.11 ± 70%
Nitrogen oxides	0.28 ± 15%
Nonmethane hydrocarbons	50 ± 48%
Carbon monoxide	1,400 ± 19%
Chemical substances	
Hydrogen	120 ± 39%
Hydrogen sulfide	30 ± 82%
Carbon disulfide	30 ± 76%
Carbonyl sulfide	10 ± 99%
Carbon black	0.11 ± 70%
Methane	25 ± 47%
Acetylene	45 ± 48%
Ethylene	1.6 ± 85%
Propane	0.23 ± 100%
Isobutane	0.1 ± 80%
Polycyclic organic material	0.002 ± 52%
Trace elements	<0.25

[a] Main process vent.

[b] Particulate matter is carbon black.

Table 10 shows the Source Severities for each of these emissions, and the uncertainty in Source Severity. Two cases are shown. Case I represents the Source Severity calculations assuming no plume rise from the main process vent. The effective stack height was assumed to be the only physical stack height of 25 meters. Case II is based on an effective stack of 36.5 meters. This includes the physical stack height of 25 meters and a plume rise of 11.5 meters based on Brigg's equation.

TABLE 10. CARBON BLACK SOURCE SEVERITIES[a]

Material emitted	Source severity (S_C)[d]	Uncertainty in source severity (S_T)[e]
Case I[b]		
Carbon monoxide	1.8	$0.09 \leq S_T \leq 36$
Particulates	0.02	$0.001 \leq S_T \leq 0.4$
Hydrogen sulfide	20	$1.0 \leq S_T \leq 400$
Case II[c]		
Carbon monoxide	0.36	$0.07 \leq S_T \leq 1.9$
Particulates	0.004	$0.0008 \leq S_T \leq 0.02$
Hydrogen sulfide	4.0	$0.8 \leq S_T \leq 20.8$

[a] Main process vent.

[b] Assuming no plume rise.

[c] Using a plume rise of 11.5 meters.

[d] S_C = calculated value of source severity.

[e] S_T = true value of source severity.

Note that when plume rise is used, the magnitude of Source Severity and the uncertainty in Source Severity decrease. Not using plume rise in Source Severity is a worst case analysis in that it overestimates Source Severity. However, it does this at the expense of increasing uncertainty.

Summary

This paper presented a discussion of the steps involved in performing a Source Assessment, decisionmaking information used by IERL and an example of the effect of data uncertainty on IERL decisionmaking. Input from engineers, sampling and analysis personnel, health effects experts and meteorologists have significant impact on IERL decisionmaking. The relationship of these inputs to IERL decisionmaking were presented.

HEALTH RELATED PROGRAMS

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Abstract

The growing concern for human health safety due to the ever increasing presence of a wide variety of chemicals in our environment has been amplified by studies showing strong associations between chemical carcinogenesis and mutagenesis. The diversity of genotoxic insults inflicted by environmental chemicals and the need to evaluate a large number of chemicals and complex mixtures has resulted in the use by this laboratory of a multi-level approach employing a battery of tests at each level. The emphasis in the Level I battery is on the detection of acute toxicity using mammalian cells in culture and intact animals and primary DNA damage and point mutation using microbial species. The Level II battery is designed to verify the results from Level I tests by employing bioassays involving mammalian cells in culture, plants, insects, and short-term tests in intact animals. The emphasis in Level III tests is on quantitative risk assessment using conventional toxicological methods.

Introduction

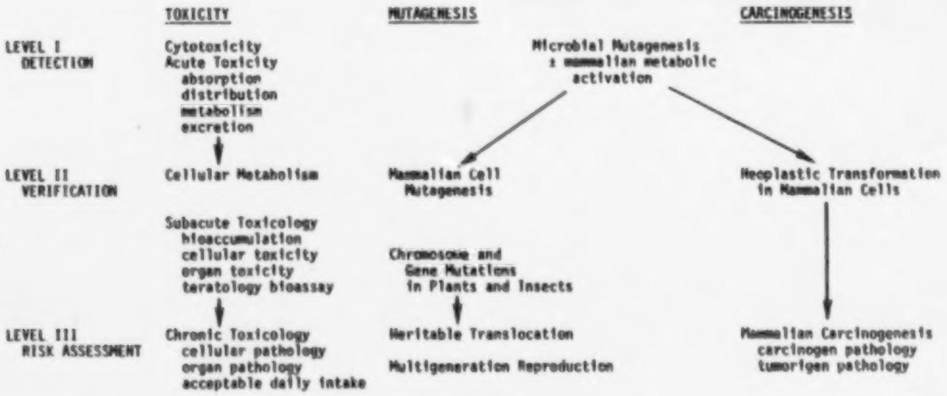
There has been a widespread concern for the last two decades about the progressively deteriorating quality of our environment. A recent article in Science(15) estimates about 63,000 chemicals in common use. Research over the past 10 years has established that a significant proportion of these chemicals is capable of causing genetic abnormalities including birth defects, carcinogenesis, and mutagenesis. In addition, environmental chemicals may be adversely affecting more subtle attributes of life such as aging, cardiovascular functions, immunity to diseases and behavior.

These toxicants occur in various products and media including foods, drugs, cosmetics, pesticides, household and industrial chemicals, as well as pollutants of air and water. The Food and Drug Administration estimates approximately 4,000 active ingredients in drugs, 2,500 additives to increase nutritional value in food, and about 3,000 chemicals used to "enhance the quality of life". The Environmental Protection Agency estimates about 1,500 active ingredients in pesticides(15). At present, only a very small proportion of these chemicals have been evaluated in terms of their potential long-term effects on the human population.

It is recognized that the toxicological effects which can be produced by environmental chemicals are numerous and yet the specificity of chemical structure and conformation make it possible for one effect to be produced exclusively. In the past, toxicologists have relied on animal bioassays to evaluate the safety of the chemicals for human health. This conventional methodology must be relied upon for purposes of risk assessment. However, comprehensive animal tests are expensive, costing $100,000 to $300,000; and time consuming, lasting from one to two years. In addition, the animal systems have their own limitations, most importantly experimental population size.

In response to the need for testing a wide variety of chemicals and complex mixtures for toxic and genotoxic effects, the Health Effects Research Laboratory, Research Triangle Park, N.C. (HERL-RTP) of the Environmental Protection Agency has adopted a matrix of bioassays based on the use of micro-organisms, plants, mammalian and human cells in culture, and whole animals. This program is briefly outlined in Fig. 1.

FIGURE 1. LEVEL APPROACH TO SCREENING FOR ENVIRONMENTAL HEALTH EFFECTS


TOXICITY
MUTAGENESIS
CARCINOGENESIS
LEVEL I
DETECTION
Cytotoxicity
Acute Toxicity
absorption
distribution
metabolism
excretion
Microbial Mutagenesis
± mammalian metabolic
activation
LEVEL II
VERIFICATION
Cellular Metabolism
Mammalian Cell
Mutagenesis
Neoplastic Transformation
in Mammalian Cells
Subacute Toxicology
bioaccumulation
cellular toxicity
organ toxicity
teratology bioassay
Chromosome and
Gene Mutations
in Plants and Insects
LEVEL III
RISK ASSESSMENT
Chronic Toxicology
cellular pathology
organ pathology
acceptable daily intake
Heritable Translocation
Multigeneration Reproduction
Mammalian Carcinogenesis
carcinogen pathology
tumorigen pathology

The testing procedures adopted by HERL-RTP for use with environmental emissions and effluents could be grouped into two major catagories: (1) those dealing with genetic toxicology and (2) those related to general toxicology. For the purpose of this report, the bioassays dealing only with cytotoxicity and genotoxicity are discussed.

The screening program for genotoxic effects is based on a stepwise or multi-level approach. This scheme involves the evaluation of suspect substances by beginning with the least expensive and most rapid assays, mostly qualitative or semi-quantitative in nature, followed by more expensive and time-consuming assays, mostly quantitative in nature.

The emphasis in Level I testing for mutagens and potential carcinogens is on detection. False negatives are of great concern, hence the requirement for a battery of tests. False positives are of lesser concern since they will likely be eliminated in higher levels of testing.

At Level I, simple *in vitro* assays for mutagenesis and potential carcinogenesis employ microbial indicator strains with and without exogenous mammalian microsomal activation systems.

It has become apparent that a majority of the genotoxins are procarcinogens or promutagens which must be converted in *in vitro* into their reactive forms before their effects can be evaluated. The metabolic conversion is believed to be mediated by oxidative enzymes and involve the formation of reactive electrophilic metabolites which interact with DNA. Although there has been controversy as to the best mode of coupling the animal metabolic activation with the *in vitro* testing systems, due mainly to differences in species, sex, age, and organ specificity for different classes of chemicals, a post-mitchondrial mammalian liver microsomal preparation (S-9) is routinely added to the test system.

Level II testing emphasizes verification of Level I results in appropriate test cells or organisms. The end points of mutagenesis and potential carcinogenesis are now separated for greater end point definition. Mutagenesis tests in Level II involve use of mammalian cells in culture (e.g. L5178Y - mouse lymphoma cells, CHO - Chinese hamster ovary cells, V79 - Chinese hamster lung cells), plants (e.g. *Tradescantia pallasada*), or use of insects (e.g. *Drosophila melanogaster*). Carcinogenesis testing *in vitro* involves morphologic cellular neoplastic transformation studies (e.g. Syrian hamster embryo cells, and BALB/c 3T3 or C3H10T1/2 mouse fibroblasts). Other relevant end points such as tests for DNA repair (unscheduled DNA synthesis) are also used in carcinogenesis screening at Level II.

The other major area of investigation under the program is that of general toxicity. It is not possible to replicate *in vitro* all of the manifestations of toxic response observed *in vivo*. For this reason we must rely on the use of the intact animal in toxicity screening. Certain *in vitro* systems are, however, useful in cytotoxicity screening. In studies on airborne particulate material, the rabbit alveolar macrophage system developed in this laboratory[30] appears to have unique applicability. This cell type is largely responsible for the removal of particulate material from the lung. Hence, in theory, any substance which alters its functional integrity could influence respiratory pathophysiology. The strain WI-38 human lung fibroblast has been employed in general toxicity evaluations under this program and has been used elsewhere to study damage and repair of DNA. A cellular toxicity test system now under development involves cultivation of primary rat liver cells. This system offers valuable screening possibilities since the liver is the principal metabolic organ in the body and is vital in the detoxification of hazardous chemicals. Such a cell system might be used at Level II for toxicity evaluations or to provide metabolic activation for other indicator organisms (e.g. when co-cultivated with *Salmonella typhimurium*).

Level III testing involves the use of conventional whole animal methods. Emphasis is placed on quantitative risk assessment in all toxicological procedures. In mutagenesis studies the emphasis is on genetic alterations induced in mammalian germinal tissues (e.g. dominant lethal test or heritable translocation test in mice). In carcinogenesis studies lifetime exposures (e.g. 2-year feeding studies in rats) are used to detect and quantify neoplasia in mammals. Conventional chronic toxicity studies in mammals are also employed at Level III.

These conventional whole animal tests should be used in conjunction with the simpler *in vitro* and submammalian tests to provide the required validation of positive results in screening tests. However, because many substances will have been eliminated in screening tests, the number of substances which must be evaluated by conventional methods will have been drastically reduced. Likewise, the total cost of toxicological evaluation will have been greatly reduced. The implementation of screening tests by industry early in the development of new chemical substances or in the pilot plant stages of new process technology may be expected to reduce the production of hazardous substances and thereby reduce or prevent their release to the environment.

Level I Bioassays

A battery of tests for this level is illustrated in Fig. 2. Again, the emphasis in Level I testing is on *detection* of mutagens, potential carcinogens and acutely toxic chemicals. This level consists of a battery of *in vitro* and *in vivo* tests. The *in vitro* end points which are considered based upon the current level of development of bioassay systems are point mutations, primary DNA damage, and cytotoxicity. All bioassays are performed with and without the presence of mammalian metabolic activation enzymes where feasible. The results obtained from Level I tests are used to assign priorities for further testing. Conventional rodent acute toxicity tests are also considered essential at Level I in view of the limitations of cytotoxicity screening tests discussed below.

FIGURE 2. LEVEL 1 BIOASSAYS FOR EVALUATING HEALTH EFFECTS

POINT EVALUATIONS

- SALMONELLA MICROSOME (AMES) REVERSE MUTATION, PROTOTROPHY TO HISTIDINE
- ESCHERICHIA COLI-WP2-MICROSOME REVERSE MUTATION, PROTOTROPHY TO TRYPTOPHANE
- SACCHAROMYCES CEREVISCIAE REVERSE AND FORWARD MUTATION

PRIMARY DNA DAMAGE

- ESCHERICHIA COLI POL A^- REPAIR DEFICIENT STRAINS
- BACILLUS SUBTILLIS, REC^- REPAIR DEFICIENT STRAINS
- SACCHAROMYCES CEREVISCIAE GENE CONVERSION AND MITOTIC RECOMBINATION

CYTOTOXICITY

- RABBIT ALVEOLAR MACROPHAGE (FOR PARTICULATES) CHINESE HAMSTER OVARY CELLS
- WI-38 HUMAN FIBROBLASTS

ACUTE TOXICITY

- 14 DAY STUDY IN RODENTS

Bioassays to Detect Point Mutation

Salmonella typhimurium (Ames test). Developed by Bruce Ames(2), this bioassay is the most extensively used as a mutagenesis prescreen to assign priorities for further testing. The *Salmonella* mutagenesis/microsome test is a *reverse* mutation assay measuring reversion to histidine independence. The experimental procedures normally employed include the spot test, the plate incorporation test, and the liquid suspension test. The five strains commonly used in the bioassay have been extensively engineered to increase their sensitivity for measuring point mutations over a wide range of test substances.

Specific Advantages:

1. Useful as a tool in rapidly obtaining information about the potential mutagenic/carcinogenic activity of uncharacterized compounds in complex mixtures. Has been applied to cigarette smoke condensate and fractions, hair dyes, soot from city air, etc.

2. Valuable as a bioassay to direct the chemical fractionation and identification of mutagenic components in complex mixtures.

3. Known human pure chemical carcinogens are positive. These include β-naphthylamine, benzidine, bis-chloromethylether, aflatoxin-B, vinyl chloride, 4-amino-biphenyl.

4. Reliable: (in testing known carcinogens and noncarcinogens) false positives, $\leq$10%; false negatives $\leq$10%.

5. Has extensive data base.

6. Tester strains extensively engineered to enhance sensitivity.

7. Results in different tester strains provide information about the mechanism of mutation (e.g. frameshift *vs* base pair substitution).

Specific Limitations:

1. Test is considered qualitative in nature.

2. Test is not responsive to metals, chlorinated hydrocarbons (long chain), asbestos and like particles.

3. Sample must be sterile. (Problems in sterilization of samples.)

4. Highly toxic components of complex samples may mask mutagenic properties of other chemicals.

5. Organic solvents used in chemical fractionation may be mutagenic (e.g. methylene chloride) and therefore may require removal (e.g. by solvent exchange) prior to bioassay.

Escherichia coli WP2. Developed by Bridges(4) and his associates in the United Kingdom, this is also a reverse mutation assay which measures prototrophy to the amino acid tryptophan. DNA repair deficiency has been included in the testor strains to enhance their sensitivity. The bioassay has been adopted for spot test, plate incorporation test, and liquid suspension assay.

Specific Advantages:

1. Can be employed to detect certain classes (e.g. nitrofurans) of chemical compounds missed by non-plasmid containing strains of *Salmonella*.

2. Has a better resolving ability than *Salmonella* in distinguishing between specific revertants and suppressor mutants.

3. Adequate data base is present.

Specific Limitations:

1. The bioassay is less sensitive than *Salmonella* due to the lack of cell wall mutants and incorporation of R-plasmids in the latter.

2. It detects only base-pair substitutions. It is deficient in the detection of frame-shift mutagens.

The following advantages and limitations are common to both the *S. typhimurium* and *E. coli* as mutagenicity test systems.

Advantages:

1. Genetically well defined.

2. Inexpensive, simple and rapid.

3. Analysis of large populations over many generations.

4. Genetic damage readily detected.

Limitations:

1. Organization of genetic material different from higher life forms.

2. No mitosis or meiosis.

3. Chromosomal damage not detected.

4. Results mostly qualitative in nature.

5. No endogenous metabolic activation.

Saccharomyces cerecisiae. Developed by F. K. Zimmerman(31) with further development by Brusick and Mayer(5), *Saccharomyces* may be used both for forward and reverse mutation assays. Forward mutation can be detected by the loss of function as a change in color of cell colonies from red to white or pink. The advantage of forward mutational assays is that mutational events at several loci can be detected. Reverse mutation experiments are easy to perform. However, the major drawback with reverse mutation is that it requires a specific genetic alteration for the restoration of function. Not all mutagens induce all possible types of alterations. As a result, reverse mutational assays may be more limited in applicability.

Advantages:

1. Eukaryotic organism, with genetic organization similar to that of higher life forms.

2. Point mutations and small chromosomal deletions may be detected.

3. Rapid, simple, and inexpensive.

4. Meiosis observable under well defined conditions.

Limitations:

1. Problems with coupling of mammalian metabolic activation systems.

2. Lack of genetic engineering to enhance sensitivity.

Bioassays to Detect Primary DNA Damage

These tests provide an indirect measure of damage to DNA from environmental toxicants.

The rationale for adopting these methods as indicators of genotoxicity is based on the recent findings that many manmade and naturally-occurring substances which have capacity to interact with DNA, through electrophilic attack, have potential to induce mutation(17).

For lack of better understanding of mechanisms and resolution of end points; the following bioassays are included in this catagory.

Escherichia coli, Pol A^{-}. Developed by Herbert Rosenkranz(25), the assay measures the differential killing between DNA repair proficient *E. coli* strain (W3110, Pol A^{+}) and DNA repair deficient strain (P3478, Pol A^{-}) as affected by environmental toxicants. Spot test and liquid suspension test procedures are employed.

Advantages:

1. The assay is well suited for detecting chemicals causing frame shift mutations.

2. Adequate data base is present.

Limitations:

Tester strains are not extensively engineered to increase sensitivity.

Bacillus subtilus rec^{-} assay. Developed by T. Kada in Japan(12), this bioassay also measures the differential killing between recombinational DNA repair proficient strain GSY 1035 (rec^{+}) and repair deficient strain 45 (rec^{-}). The most commonly used procedure is the spot test. Usually both bacterial strains are streaked out along intersecting lines. The test chemical is spotted at the intersection. This affords a direct comparison of the zone of inhibition between the repair proficient and deficient strains on one plate. The basic difference between *B. subtilus* rec^{-} assay and *E. coli* A^{-} lies in the defects in the respective repair systems involved.

Advantages:

1. Very rapid and simple bioassay.

2. Highly versatile.

Limitations:

1. Requires fairly large amount of test substance.

2. Not suitable for substances that do not diffuse rapidly in agar.

Saccharomyces cerevisiae - Gene Conversion and Mitotic Recombination. Mitotic recombination of the reciprocal type, mitotic recombination, and the non-reciprocal type, mitotic gene conversion, provide convenient markers for assessing the DNA damaging potential of environmental chemicals. The degree of mitotic crossing over is evaluated by the frequency of twin spot sectors and that of mitotic gene conversion by the differential growth in a selective medium.

Advantages:

1. Diploid cells with eukaryotic chromosomal organization.

2. Rapid and inexpensive assay.

Limitations:

1. Less versatile due to problems associated with cell wall permeability.

2. Problems associated with coupling of metabolic activation with the assay.

3. Inadequate data base showing the reliability of this assay system.

Bioassays For Assessing Cytotoxicity

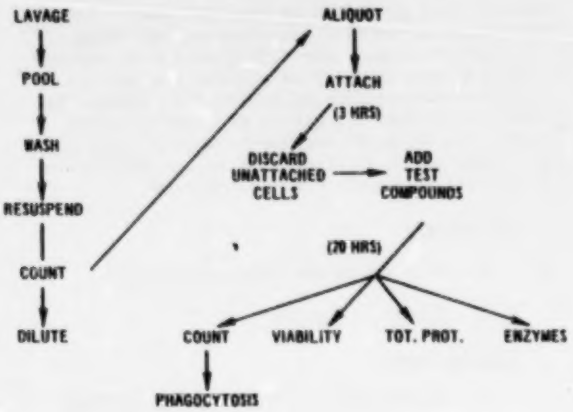
The HERL-RTP has employed three assays to evaluate the cytotoxicity of parent chemicals, metabolites and complex environmental mixtures.

These include (1) the rabbit alveolar macrophage (RAM), (2) proliferating cultures of Strain WI-38 human lung fibroblasts and (3) clonal assays employing continuous rodent cell lines such as the Chinese hamster ovary (CHO) cell line.

Rabbit Alveolar Macrophage (RAM) Assay

The basic methodology for this assay is illustrated in Fig. 3.

FIGURE 3. RABBIT AVEOLAR MACROPHAGE (RAM) TEST SYSTEM



Alveolar macrophages obtained by saline lavage from lungs of rabbits are maintained in tissue culture and exposed to particulate materials, soluble chemicals or gases. The end points measured include cell numbers, cell viability, adenosine triphosphate (ATP) levels, phagocytic activity, etc.

Advantages:

1. Test indicates potential for pathophysiological damage to pulmonary cell systems and impaired lung defense against inhaled particulate materials.

2. Particulates such as silica and asbestos, soluble and insoluble metallic compounds, and oxidant gases have demonstrated cytotoxic activity *in vitro* and *in vivo*.

3. It has been possible to "rank" crude particulate materials according to relative toxicity based upon concentration-response data.

Limitations:

1. Protective influences of the intact animal may not be reflected *in vitro*.

2. Cells are non-dividing and cannot be maintained in continuous culture.

Human Lung Fibroblast (WI-38) Assay. These diploid cells of human origin have been used effectively for determining the cytotoxicity of environmental toxicants. These cells exhibit major pathways of macromolecular synthesis common to all dividing cells. Growth inhibition is commonly used as a measure of cytotoxicity in this system.

Clonal Toxicity (e.g. CHO system). The impairment in the clonal growth of continuous rodent cell lines after treatment with a test substance is used as a criterion of cytotoxicity.

Advantages and Limitations of Cytotoxicity Tests. These assays are less expensive, more rapid and require less samples than conventional whole animal bioassays. The assays are used to provide preliminary information on the relative cellular toxicity of unknown samples. The basic disadvantage of these assays is that they do not represent intact animals and therefore provide only preliminary information about the potential health hazards of the test chemicals.

Level II Bioassays (In Vitro and In Vivo)

The Level II test battery, illustrated in Fig. 4, is designed to verify the results obtained in Level I bioassays. The test systems are selected to provide information on primary DNA damage, point mutations, chromosomal aberrations and cellular neoplastic transformation. The test organisms are mammalian cells in culture supplemented with exogenous metabolic activation, plants, insects, and whole animals, to provide greater relevance to the human situation.

FIGURE 4. LEVEL 2 BIOASSAYS FOR HEALTH EFFECTS

PRIMARY DNA DAMAGE

- UNSCHEDULED DNA SYNTHESIS-WI-38
- SISTER-CHROMATED EXCHANGE FORMATION (*IN VITRO* AND *IN VIVO*)

POINT MUTATION

- MAMMALIAN CELLS IN CULTURE
- INSECTS-DROSOPHILA
- PLANT-TRADESCANTIA AND MAIZE

CHROMOSOMAL ABERRATIONS

- *IN VITRO* CYTOGENETICS - MAMMALIAN CELLS IN CULTURE
- *IN VIVO* CYTOGENETICS - LYMPHOCYTIC CULTURE AND BONE MARROW CELLS

NEOPLASTIC TRANSFORMATION

- SYRLIAN HAMSTER EMBRYO SYSTEM
- MOUSE FIBROBLAST CELL LINES

TERATOGENESIS STUDIES

SUBACUTE STUDIES IN RODENTS

Bioassays to Detect Primary DNA Damage

WI-38 - unscheduled DNA synthesis. Developed by Stich(28), this assay evaluates the test compounds for their ability to induce unscheduled DNA synthesis (UDS) in human diploid WI-38 fibroblasts blocked in G_1 phase.

Advantages:

DNA repair can be measured in human cells in culture. Similar studies can be performed using peripheral leucocytes in animals permitting comparison between *in vitro* and *in vivo* exposures to carcinogens or mutagens.

Limitations:

1. The precise type of molecular binding between carcinogens and DNA which triggers excision repair is unknown.

2. DNA repair synthesis does not measure residual damage to DNA.

Sister-Chromatid Exchange Formation (SCE). Developed by Sam Latt(14), the SCE involves a reciprocal exchange between sister-chromatids which does not result in change in overall chromosomal morphology. The technique depends upon a differential stainability of sister-chromatids by exposing cells to 5-bromodeoxyuridine (BudR) through two successive cell generations. Subsequent staining with fluorochrome and/or Giemsa readily demonstrates the number of times per cell where darkly-staining chromatids are exchanged with lightly-staining chromatids.

The assay may be used either in the *in vitro*(20,21,29) or *in vivo* situation(1).

Advantages:

The test is an inexpensive, sensitive and a rapid method of measuring the effect of a substance on chromosomes.

Limitations:

1. The mechanism and significance of SCE is not well understood.

2. No clear relationship between SCE and chromosomal breaks has been established.

3. BudR which forms the basis of differential staining in this bioassay is itself a mutagen. Therefore, it is difficult to evaluate the synergistic, antagonistic or interactive effects of BudR with the test compounds.

Bioassays to Detect Point Mutation

Mammalian Cell Mutagenesis In Vitro. There are three mammalian cell mutagenesis bioassays which are commonly used:

L5178Y Mouse Lymphoma

Developed by Donald Clive(7), this is a forward mutation assay which measures the mutational induction of thymidine kinase (TK) deficiency from TK competent heterozygotes using a selective medium. The TK locus is believed to be autosomal.

Chinese Hamster Cells

There are two assay systems derived from Chinese hamsters: Chinese hamster ovary cells (CHO) developed by Hsie and associates(18,19) and Chinese hamster lung cells (V79) developed by Chu(6) and Krahn and Heidelburger(13). Both assays measure resistance to drugs at the hypoxanthine-guanine-phosphoribosyltransferase (HGPRT) and ouabain loci. These loci are assumed to be X-linked. The HGPRT locus is better characterized and considered to be more sensitive than the ouabain locus.

Advantages:

1. The full range of mutation responses of somatic cells observable, not just point mutations.

2. Faster, less expensive than *in vivo* assays.

3. Can be coupled with *in vitro* metabolic activation system from various sources.

4. Mutations measured in cultured mammalian cells are more relevant to the intact mammal than in bacterial systems.

5. Responds to particulates (asbestos).

6. May offer better quantitative correlation with carcinogenicity than does mutagenicity data of *Salmonella*, though this is very preliminary.

Limitations:

1. The cell line used for experimentation are transformed lines and therefore do not represent "normal" cells.

2. These cells do not undergo meiosis.

3. Only one or two loci from the entire genome are monitored.

4. Cells have limited endogenous metabolic activation capability.

5. There are some doubts about the genetic nature of the events observed at certain loci.

***Tradescantia* Stamen-hair.** Developed by A. H. Sparrow(27), this plant provides a unique screening system for mutagenesis. The clones heterozygous for stamen hair color are exposed to test substances and a change of stamen hair cells from blue to pink coloration is recorded as a mutational event.

Advantages:

1. The *Tradescantia* stamen hair system is very sensitive to physical and chemical mutagens.

2. Easy to handle.

3. Has eukaryotic chromosomal organization.

4. Suitable for *in situ* testing.

5. Suitable for testing liquid and volatile compounds.

Limitations:

1. Stamen-hair cells are somatic cells and therefore do not provide the information on the influence of test compounds on the germinal cells.

2. Nature of mutational events in this system is not well understood.

3. To date, the data base on this system is very meager.

Sex-linked Recessive Lethal in *Drosophila*. The sex-linked recessive lethal test in *Drosophila* is a relatively economical and sensitive test for the evaluation of environmental chemicals for potential health effects in higher organisms. This system is capable of detecting mutations at approximately 1,000 loci on the X chromosome.

Advantages:

1. A large number of the test organisms can be reared easily and economically.

2. Provides the advantages of endogenous metabolic activation.

3. Genotoxic effects are evaluated in the germ cells.

4. Many loci in the genome can be monitored at the same time.

Limitations:

1. *Drosophila* does not activate some polycyclic hydrocarbons.

2. Several classes of chemicals including certain insecticides cannot be evaluated in the *Drosophila* system.

Assays to Detect Chromosomal Aberrations.

Test systems to evaluate chromosomal abnormalities should be an integral component of a scheme designed to evaluate the genotoxic effects of toxicants. Many types of cancer and several catagories of birth defects are related to the structural and/or numerical changes in the chromosomal complements of animals.

Both *in vitro* and *in vivo* bioassay are currently employed to determine the ability of environmental chemicals to cause chromosomal abnormalities.

In vitro cytogenetic studies to detect numerical and structural chromosomal alterations can be performed with the mammalian tumor lines, Muntjack or Chinese hamster(10). *In vivo* studies include short term (48 to 72 hours) culture of lymphocytes(8) and micronucleus formation in bone marrow cells(23) derived from exposed animals.

The micronucleus assay is based on the observations that small pieces of chromatin material without centromeres are produced as a result of chromosomal breaks and can be easily identified in the interphase. The assay is relatively simple, rapid, and inexpensive.

Limitations:

Chromosomal alterations are relatively less sensitive indicators of genotoxic effects than point mutations.

Oncogenic Transformation

Oncogenic transformation is the process whereby normal cells grown in culture are converted into malignant cells after treatment with an oncogen. The demonstration of malignancy (tumor formation) can be observed by injecting the transformed cells into whole animals. A number of mammalian oncogenic transformation bioassays utilizing cells derived from different rodent species are currently available. Some of these cell systems have the endogenous capability to activate procarcinogens while with others exogenous metabolic activation has been used successfully.

Two types of assay systems in use for oncogenic transformation are: (1) Syrian hamster embryo system and (2) mouse fibroblast cell lines. The Syrian hamster embryo system(9), utilizes primary cells which are diploid and retain high metabolic activation capability, thereby providing more relevance to human conditions.

Mouse embryo cell lines are continuous cell lines with aneuploid chromosomal complements. The tester strains have limited metabolic activation ability. These systems are easily adaptable for testing agents as initiators and promotors, cocarcinogens and carcinogens.

Advantages:

1. Bioassays using mammalian cells are considered to be directly relevant to the process of oncogenesis in experimental animals.

2. These tests are highly predictive. Few if any false positive are detected by this methodology.

Limitations:

1. The assays are relatively expensive to perform.

2. Highly trained personnel are required to perform the tests.

Level III Bioassays

Level III testing involves the use of conventional whole animal methods. The emphasis is placed on quantitative risk assessment. Experimentation with intact mammals are needed to provide information on the presence of mutagenic concentration of toxins in the target cells. In addition, information on pharmacokinetics, such as absorption, distribution, metabolic transformation, and excretion cannot be obtained without studies on mammals(26).

Heritable Translocation Test. The heritable translocation assay is designed to measure reciprocal translocation in the germ cells of treated animals, usually the male mice. The presence of induced translocations can be observed by mating the F_1 male progeny of the treated males with the untreated females(24,11).

Advantages:

1. Chromosomal effects detected in the

progeny of treated animals demonstrating a heritable effect.

2. Effects can be confirmed by examination of germinal tissues.

3. Metabolism more similar to that in man.

Limitations:

1. Poorly defined genetically.

2. Genetic damage not readily detectable.

3. Delayed mutant expression time.

4. Small populations and few generations amenable to analysis.

5. Expensive.

Dominant Lethal Test

The genetic basis for dominant lethal test is the induction of chromosomal damage and rearrangements resulting in nonviable zygotes(11). The genetic damage is detected as pre-implant loss of non-viable blastocysts and early embryonic death.

Advantages:

Produces general information about effects of a substance on the germ cells of the test animals at a relatively low cost.

Limitations:

The bioassay is incapable of detecting certain weak mutagens.

Carcinogenesis and Tumorigenesis in Intact Animals

These tests are essential in evaluating risk to human health. However, the very high cost and long study period required for these tests, limit their utility.

Resource Implications

The resource implications of carcinogenicity/-mutagenicity testing programs are shown in Table 1. It is evident that most of the short-term bioassays assigned to detect primary DNA damage and point mutation are relatively rapid, inexpensive, and require small amounts of test material.

Table 2 presents a summary of resource requirements for each level of testing. Levels I and II test batteries could be applied at a cost of $35,000 and tests completed within three months, whereas, a battery of Level III bioassays would be approximately 8 to 10 times more costly in terms of dollars and time.

Summary

Considering the advantages and limitations of the assays discussed, it is evident that no single method is entirely adequate in assessing the toxicity and genotoxicity of environmental chemicals and complex mixtures. This fact supports the adoption of a multi-level approach with batteries of tests at each level. Such an approach is cost and resource effective.

Table 1

Resource Implications of Carcinogenicity-Mutagenicity Program

Test	$ Cost[1]	Study time[2]	Quantity of material required
	Gene (Point) Mutations		
Bacteria (Ames Plate Test)	350 - 600	2-4 weeks	2 g
Bacteria (Liquid Suspension)	1,000 - 2,000	2-4 weeks	2 g
Eukaryotic micro-organisms (yeast)	200 - 500	2-4 weeks	2 g
Insects (*Drosophila*, recessive lethal)	6,000 - 7,500	4-6 months	10 g
Mammalian somatic cells in culture (mouse lymphoma)	2,500 - 4,800	1-2 months	2 g
Mouse Specific Locus	20,000+	1 year	25 g
	Chromosomal Mutations		
In vivo cytogenetics	3,000 - 6,500	6-8 weeks	20 g
Insects, heritable chromosomal effects	3,000 - 6,500	4-6 weeks	10 g
(*Drosophila*) non-disjunction	3,000	1-3 months	
Dominant lethal in rodents	6,000 - 10,000	3 months	20-25 g
Heritable translocation in rodents	40,000 - 67,000	12-18 months	25 g
	Primary DNA Damage		
DNA repair in bacteria	200 - 500	2-4 weeks	2 g
Unscheduled DNA synthesis	350 - 2,000	4-6 weeks	2-5 g
Mitotic recombination and/or gene conversion in yeast	200 - 500	4-6 weeks	2-5 g
Sister chromitid exchange	1,000 - 1,200	4-6 weeks	2-5 g
In vitro Transformation	6,500 - 7,500	10-12 weeks	2-5 g

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1. Cost of these tests has varied and can be expected to vary until test requirements are stabilized.
2. This time period covers the experimental time and report preparation.

Table 2

Relative Cost, Study Time and Quantity of Material Required for the Implimentation of Testing for Mutagenicity Carcinogenicity Program

Level	Number of tests	Approximate cost	Study time	Quantity of material required
I	8	$ 3,300-5,000	4-6 weeks	2-5 g
II	9	$27,000-30,000	6-12 weeks	5-20 g
III	2	$200,000-300,000	1-2 years	25-30 g

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BIOLOGICAL TESTING METHODOLOGY

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Abstract

Biological procedures for testing feedstocks and waste streams of individual processes have been developed as part of EPA's phased approach to Environmental Source Assessment. The objectives of the first phase or level of biological testing are to (1) provide preliminary data on the biological effects of feedstocks and waste streams, (2) identify problems in implementing the tests on the streams, and (3) prioritize the streams according to their relative hazard. The Bioassay Subcommittee of IERL-RTP's Environmental Assessment Steering Committee has developed a Level 1 biological test protocol to meet these objectives. The protocol includes four health tests and eight ecological tests to be implemented on liquid, solid, and gaseous streams. Pilot studies are underway to test and refine this protocol. Results indicate the phased approach is effective in directing environmental assessment activities.

Introduction

Environmental source assessment, as conceived by the Industrial and Environmental Research Laboratory of the Environmental Protection Agency at Research Triangle Park, North Carolina (IERL-RTP), involves the testing of feedstocks and waste streams associated with energy or industrial processes in order to define control technology needs. Four goals are recognized for environmental source assessment Programs:(1)

- Evaluation of physical, chemical, and biological characteristics of all process streams
- Prediction of environmental effects
- Prioritization of streams relative to hazard
- Identification of control technology programs.

Biological testing, along with physical and chemical analyses, provides the information needed to meet the first three goals. The unique contributions made by biology to environmental assessment include the direct measurement of toxicity of process streams to the test organisms and the detection of synergistic or antagonistic effects often characteristic of complex chemical mixtures. The objective of this paper is to provide an overview of the bioassay protocol used in environmental assessment and give an example demonstrating the application of this protocol.

Phased Approach

The biological, chemical, and physical data requirements for environmental assessment are considerable. IERL-RTP has developed a phased approach to environmental assessment to efficiently organize the data collection and analysis efforts. The phased approach may be characterized as both comprehensive and cost-effective.(1) It is comprehensive in that all feed and waste streams are tested. It is cost-effective because the analytical procedures are implemented sequentially with each successive step or phase building on information gained in previous phases.

The phased approach has three levels with each level designed to achieve specific objectives (Table 1).(2) Level 1 provides a preliminary screening of all process feed and waste streams using simple, inexpensive sampling and analysis procedures. It is meant to provide qualitative or semiquantitative information on these streams so that their relative hazard may be estimated. Level 2 validates and expands on the data obtained in Level 1. The test procedures are generally more complex and costly than those used in Level 1. Level 2 efforts are focused first on those streams identified in Level 1 as being the most hazardous. Streams with low toxicity or hazard have second priority. Streams definitively classed as nontoxic (using biological, chemical, and physical analyses) in Level 1 need not be tested in Level 2. The third level deals with process variations and chronic toxicity. It is facility-specific with the test protocol tailor made for the particular facility being assessed. Currently, a sampling and analysis protocol exists for Level 1 biology. Level 2 procedures are under development but a complete protocol is not yet available. Level 3 tests are facility-specific and a test protocol can be developed only when the particular facility is identified and Level 1 and 2 testing is completed. The remainder of the discussion concerning the phased approach focuses on Level 1 biological testing.

TABLE 1. OBJECTIVES OF THE PHASED APPROACH

Level 1 -
- To provide preliminary EA data
- To identify problem areas
- To generate data for prioritization of process feedstocks and waste streams

Level 2 -
- To validate and expand information from Level 1

Level 3 -
- To monitor process and time variations in toxicity
- To monitor sublethal, chronic effects

The Level 1 bioassay protocol was developed by the Bioassay Subcommittee, a subset of EPA's Environmental Assessment Steering Committee. The protocol consists of 12 health and ecological tests which are briefly described in Table 2.

Liquids are sampled using heat exchange, tap sampling, and dipper sampling methods. The biological tests do require considerably larger volumes of liquids (~240ℓ) than do the chemical tests. Solid samples are collected using grab sampling techiques.

TABLE 2. LEVEL 1 HEALTH AND ECOLOGICAL EFFECTS

Test	Test Objective	Sample Quantity	Test Organism	Test Time	Test Results
Ames Microbial Mutagenesis	Mutagenic activity	1 g/10 ml	Salmonella typhimurium	2-4 days	+/- (mutagenecity)
Rabbit Alevolar Macrophage	Cytotoxicity	1/2 g/50 ml	Rabbit lung macrophage cells	2-4 days	EC$_{50}$
WI-38	Cytotoxicity	1/2 g/50 ml	Human lung fibroblasts	2-4 days	EC$_{50}$
Rodent Acute Toxicity	Whole animal toxocity	100 g/1 l	Laboratory rat	14 days	LD$_{50}$, necropsy observations
Freshwater Algal Assay	Toxicity	200 l	Selenastrum capricornutum	14 days	EC$_{50}$
Daphnia Static Bioassay	Acute toxicity		Daphnia pulex	4 days	LC$_{50}$
Fathead Minnow Static Bioassay	Acute toxicity		Pimephales promelus	4 days	LC$_{50}$
Marine Algal Assay	Toxicity	40 l	Skeletonema costatum	14 days	EC$_{50}$
Grass Shrimp Static Bioassay	Acute toxicity		Palaemonetes pugio	4 days	LC$_{50}$
Sheepshead Minnow Static Bioassay	Acute toxicity		Cyprinodon variegatus	4 days	LC$_{50}$
Soil Microcosm	Toxicity	1 g/ml	Intact soil system	3 weeks	DOC, Ca transport, total Ca, ATP
Stress Ethylene	Toxicity	1500 l gas	Soybean	28 hours	Ethylene production

These tests are organized into protocols that permit solid, liquid, gaseous, and suspended particulate samples to be properly analyzed (Figures 1 and 2). Level 1 samples for biological testing are collected using the procedures developed to collect Level 1 chemistry samples.(3) The Source Assessment Sampling System (SASS) is used for the particulate and sorbent (XAD-2) samples (see Figure 2). A large volume of gas (1500ℓ) is needed for Level 1 biology. Occasionally the quantity of sample available for Level 1 testing is limited, and the full biological test protocol cannot be implemented. Under such circumstances the tests have been prioritized and are implemented in the following order:

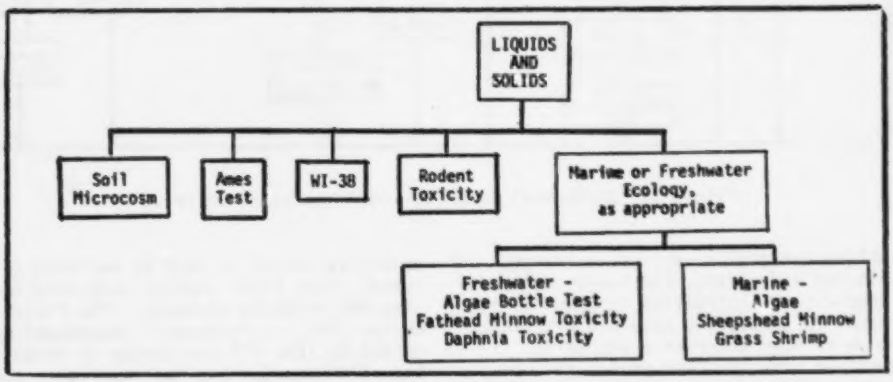

LIQUIDS AND SOLIDS
Soil Microcosm
Ames Test
WI-38
Rodent Toxicity
Marine or Freshwater Ecology, as appropriate
Freshwater - Algae Bottle Test Fathead Minnow Toxicity Daphnia Toxicity
Marine - Algae Sheepshead Minnow Grass Shrimp

Figure 1. Bioassay Protocol for Liquid and Solid Streams

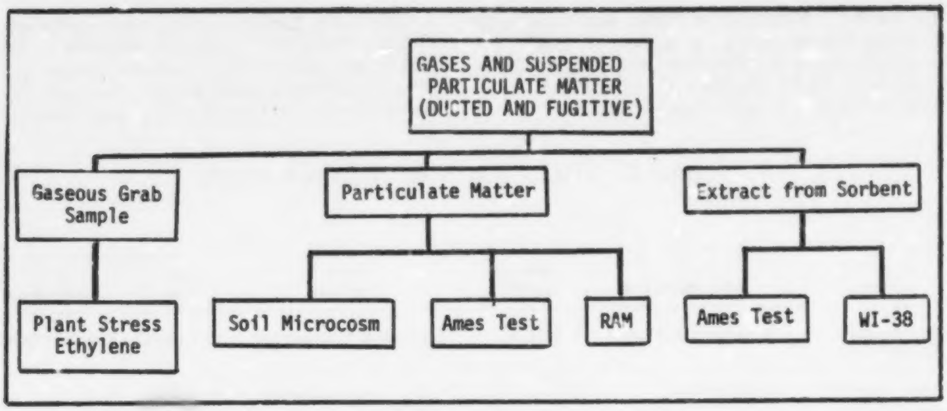

GASES AND SUSPENDED PARTICULATE MATTER (DUCTED AND FUGITIVE)
Gaseous Grab Sample
Particulate Matter
Extract from Sorbent
Plant Stress Ethylene
Soil Microcosm
Ames Test
RAM
Ames Test
WI-38

Figure 2. Bioassay Protocol for Gases and Suspended Particulate Matter Streams

1. Ames, WI-38, and RAM
2. Rodent Acute Toxicity
3. Marine or Freshwater Tests
4. Soil Microcosm

The stress ethylene test does not appear in this scheme since it is the only biological test for gaseous samples.

Many of the samples collected for the Level 1 bioassays can be tested without any processing or treatment. Others require some type of preparation before the biological tests can be performed on them (Figure 3, Preparation). Preparation procedures include extraction, solvent exchange, filtering, grinding and sizing, and aqueous extract or leachate production. Extraction is used for the SASS XAD-2 column to remove the adsorbed organics. Solvent exchange is used wherever a sample is deemed incompatible with the test procedure. Dimethyl sulfoxide (DMSO) is often used in the process. Liquids with suspended solid may require filtering before testing. Solid samples are ground to respirable size (≤ 5 μm) before being used in the health tests. Solid streams that may be subjected to leaching by surface or groundwater when they are stored or disposed are tested using the aquatic tests. Appropriate quantites of leachate are prepared using the 30-minute shake technique.(4) When the samples have been properly prepared, they are analyzed using the test protocol indicated in Figures 1 and 2.

Once developed, it was necessary to validate the bioassay protocol to determine if Level 1 objectives could in fact be met with this series of tests. Four pilot studies were selected for testing the bioassay protocol. The Fluidized Bed Combustor (FBC) environmental assessment program supported by IERL-RTP was chosen to conduct one of the pilot studies and the results of that study are reported here.

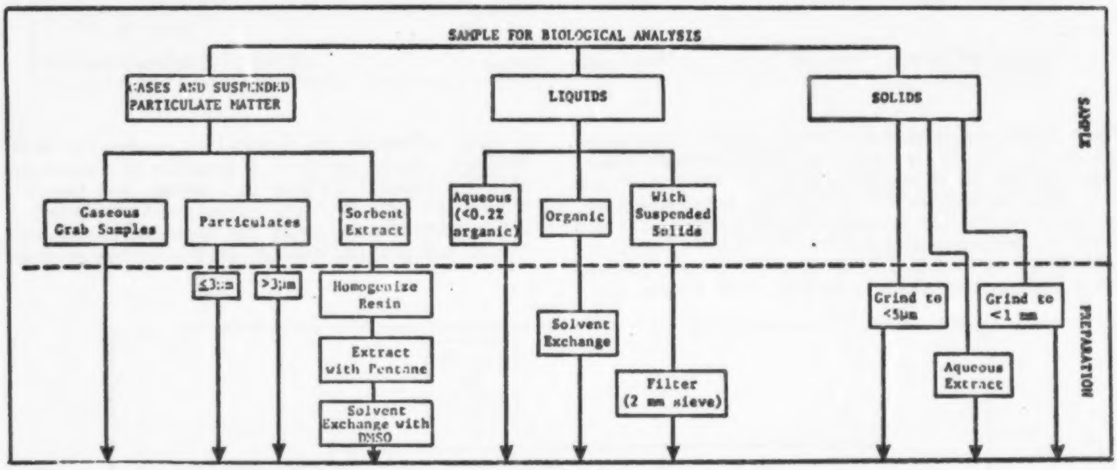

SAMPLE FOR BIOLOGICAL ANALYSIS
GASES AND SUSPENDED PARTICULATE MATTER
LIQUIDS
SOLIDS
SAMPLE
Gaseous Grab Samples
Particulates
Sorbent Extract
Aqueous (<0.2% organic)
Organic
With Suspended Solids
≤3μm
>3μm
Homogenize Resin
Extract with Pentane
Solvent Exchange with DMSO
Solvent Exchange
Filter (2 mm sieve)
Grind to <5μm
Grind to <1 mm
Aqueous Extract
PREPARATION

Figure 3. Biological Sampling and Preparation Overview

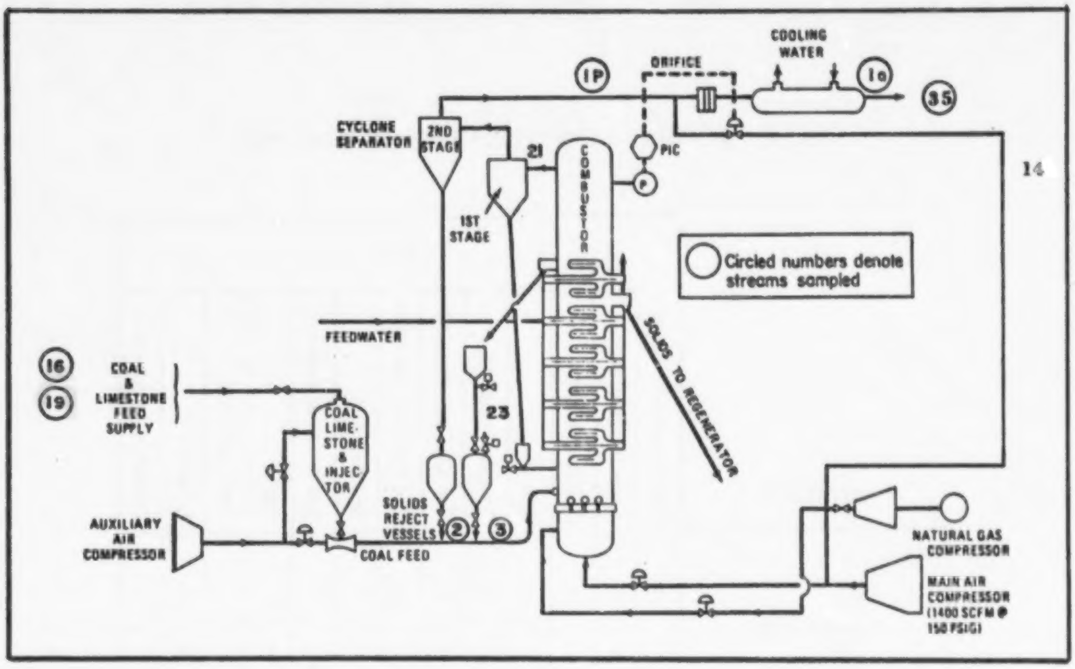
Fluidized Bed Bioassay Pilot Study(5)

The FBC bioassay pilot study was performed on samples collected from the Exxon pressurized FBC miniplant located in Linden, New Jersey and was part of the Comprehensive Analysis of this facility. The pilot study had two objectives:

1. Test the applicability of the Level 1 bioassay protocol
2. Provide Level 1 environmental data for the Exxon FBC.

Pilot study work was initiated in April, 1977 and completed in February, 1978.

A schematic of the Exxon FBC miniplant is given in Figure 4 showing the feed and waste streams. Six of these streams--the flue gas (1a and 1p), the fly ash from the second cyclone (2), the bed discard (3), the coal feed (16), the dolomite feed (19), and the slurry from the flue gas scrubber (35)--were collected using Level 1 procedures and returned to the laboratory for appropriate sample preparation. After preparation a total of 13 samples were available for Level 1 biological analysis (Table 3).


COOLING WATER
ORIFICE
1P
1a
35
CYCLONE SEPARATOR
2ND STAGE
21
PIC
P
14
COMBUSTOR
1ST STAGE
Circled numbers denote streams sampled
FEEDWATER
SOLIDS TO REGENERATOR
16
19
COAL & LIMESTONE FEED SUPPLY
COAL LIME-STONE & INJECTOR
23
SOLIDS REJECT VESSELS
2
3
AUXILIARY AIR COMPRESSOR
COAL FEED
NATURAL GAS COMPRESSOR
MAIN AIR COMPRESSOR (1400 SCFM @ 150 PSIG)

○ Circled numbers denote streams sampled, uncircled numbers were not sampled. Samples include 1a, 1p, 16, 19, 2, 3, and 35.

Figure 4. Exxon Fluidized-Bed Combustion Miniplant

The bioassay test protocol was implemented on the 13 samples from the Exxon FBC miniplant (Table 4). A total of 67 tests were required to complete the pilot study. Although only marine or freshwater tests (depending on the type of water body receiving the effluents) would normally be used for most environmental assessments, both sets of tests were employed for the pilot study in order to more fully test the validity of the bioassay protocol. The results of the tests are essentially complete and reported in Table 5.

Interpretation of the results and the prioritization of the streams according to toxicity is currently being performed by both the Bioassay Subcommittee and Battelle. Preliminary analysis indicates that the scrubber slurry and fine particulates are among the more toxic streams. The bed discard leachate was relatively toxic to terrestrial and freshwater organisms but not to saltwater species. Other samples such as the bed discard and dolomite showed very little or no toxicity. It must be stressed that biological test results and the ranking of streams are relative and determination of absolute toxicity is beyond the scope of Level 1 testing. The bioassay results have not yet been compared with those from Level 1 chemistry so no conclusions are possible concerning the possible correlation between the two types of Level 1 procedures.

TABLE 3. THE EXXON FBC STREAMS COLLECTED FOR THE PILOT STUDY AND THE THIRTEEN SAMPLES, RESULTING FROM PREPARATION PROCEDURES, WHICH WERE TESTED USING BIOASSAYS

Stream	Collection Procedure	Sample Preparation	Sample Tested
Gas			
1. Flue Gas (1 a and 1 p)	SASS (1 a)	--	1. Coarse Particulates, ≥ 3μm
	SASS (1 a)	--	2. Fine Particulates, < 3 μm
	SASS (1 a)	Sorbent Extraction	3. XAD-2 Extract in Methylene Chloride
	Grab (1 p)	--	4. Gas
Liquids			
2. Scrubber Slurry (35)	Grab	--	5. Scrubber Slurry, Aqueous
Solids			
3. 2nd Cyclone Discard (2)	Grab	Grind	6. 2nd Cyclone Discard, ≤ 5 μm
	Grab	Aqueous Leach	7. Leachate of 2nd Cyclone
4. Bed Discard (3)	Grab	Grind	8. Bed Discard, < 5 μm
	Grab	Aqueous Leach	9. Leachate of Bed Discard
5. Coal (16)	Grab	Grind	10. Coal, ≤ 5 μm
	Grab	Aqueous Leach	11. Leachate of Coal
6. Dolomite (19)	Grab	Grind	12. Dolomite, ≤ 5 μm
	Grab	Aqueous Leach	13. Leachate of Dolomite

TABLE 4. BIOASSAY TEST MATRIX FOR EXXON FBC PILOT STUDY

	SAMPLE												
BIOASSAY	Coarse Particulates	Fine Particulates	XAD-2 Extract	Gas	Scrubber Slurry	2nd Cyclone Discard	2nd Cyclone Leachate	Bed Discard	Bed Discard Leachate	Coal	Coal Leachate	Dolomite	Dolomite Leachate
Health													
1. Ames	X	X	X		X	X	X	X	X	X		X	
Cytotoxicity													
2. RAM	X	X				X		X		X		X	
3. WI-38			X		X		X		X				
4. Rodent Toxicity					X	X	X	X	X	X		X	
Ecological													
Aquatic Freshwater													
5. Algal					X		X		X		X		X
6. Daphnia					X		X		X		X		X
7. Fish					X		X		X		X		X
Saltwater													
8. Algal					X		X		X		X		X
9. Shrimp					X		X		X		X		X
10. Fish					X		X		X		X		X
Terrestrial													
11. Soil Microcosm	X	X			X	X	X	X	X	X		X	
12. Stress Ethylene				X									

TABLE 5. BIOASSAY RESULTS FOR FBC STUDY

Test	Test Parameter	Coarse Particulates	Fine Particulates	XAD-2 Extract	Gas	Scrubber Slurry	2nd Cyclone Discard	2nd Cyclone Leachate	Bed Discard	Bed Discard Leachate	Coal	Coal Leachate	Dolomite	Dolomite Leachate
Ames	+/-	+	+	NA		-	-	NA	-	-	-		-	
Cytotoxicity RAM	EC_{50}	NT	596-3000	NA		$\geq$ 146	NT	NT	NT	NT	NT		NT	
Rodent Toxicity	LD_{50}					NT	NT	NT	NT	NT	NT		NT	
Aquatic Freshwater Algal Daphnia Fish	EC_{50} LC_{50} LC_{50}					9% 31.6% 67.9%		VLT 91.6% VLT		45% 40.9% 25.3%		19% 70.9% 92.1%		VLT VLT VLT
Saltwater Algal Shrimp Fish	EC_{50} LC_{50} LC_{50}					15% 18% 70.5%		VLT 72.5% NT		NT NT NT		38% 66% 71.5%		24% 74.8% NT
Terrestrial Soil Microcosm	Ranked in order of toxicity	5	6			NT	2	3	7	1	4		NT	
Stress Ethylene	Percent of increase over control				NT									

NA = Not available.
VLT = Very low toxicity.
NT = No toxicity.

Conclusions

Preliminary results from the FBC pilot study indicate that the Level 1 biological sampling, preparation, and analysis procedures can meet the goals established for Level 1 of the phased approach. The pilot study did reveal problems with the soil microcosm and stress ethylene procedures as originally conceived and provided appropriate modifications to improve these tests. Some of the other tests received minor refinements. Minor deficiencies in sample collection and preparation procedures were also detected and suitable changes incorporated into the protocol to correct them. This evolutionary refinement of Level 1 bioassay procedures can be expected to continue as their implementation in other environmental assessment programs reveals the need. The ability to interpret the results of the bioassays and to prioritize feed and waste streams using both Level 1 biology and chemistry will also improve as more experience in testing complex mixtures is gained.

References

1. Dorsey, J.A., L.D. Johnson, R.M. Statnick, and C.H. Lockmüller. 1977. Environmental Assessment Sampling and Analysis: Phased Approach and Techniques for Level 1. EPA-600/2-77-115, June 1977. Industrial Environmental Research Laboratory, Office of Energy, Minerals, and Industry, U.S. Environmental Protection Agency. Research Triangle Park, N.C.

2. Duke, K.M., M.E. Davis, and A.J. Dennis. 1977. IERL-RTP Procedures Manual: Level 1 Environmental Assessment Biological Tests for Pilot Studies. EPA-600/7-77-043, April 1977. Industrial Environmental Research Laboratory, Office of Energy, Minerals, and Industry, U.S. Environmental Protection Agency. Research Triangle Park, N.C.

3. Hamersma, J.W., S.L. Reynolds, and R.F. Maddalone. 1976. IERL-RTP Procedures Manual: Level 1 Environmental Assessment. EPA-600/2-76-160a, June 1976. Industrial Environmental Research Laboratory, Office of Energy, Minerals, and Industry, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

4. Environmental Protection Agency. 1976. Bioassay Procedures for Ocean Disposal Permit Program. EPA-600/9-76-010. Environmental Research Laboratory, Gulf Breeze, Florida.

5. Allen, J.M., J.E. Howes, Jr., S.E. Miller, and K.M. Duke. 1977. Draft Report on Comprehensive Analysis of Emissions from Exxon Fluidized-Bed Combustion Miniplant Unit. Battelle Columbus Laboratories, Columbus, Ohio.

SOURCE ASSESSMENT SAMPLING SYSTEM-DESIGN DEVELOPMENT AND CALIBRATION

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Introduction

The Process Measurements Branch, IERL/RTP, has developed strategy for sampling and analysis in Environmental Assessment Programs. Three levels of sampling/analysis detail are specified. Level 1 measures organic and inorganic mass emissions semiquantitatively (within a factor of 2 to 3). Levels 2 and 3 provide quantitative and/or continuous monitoring of specific pollutant species.

The Source Assessment Sampling System (SASS) is the primary sampling tool for Level 1 gaseous and particulate emissions. The SASS train performs the following functions:

- Extractive sampling of gaseous streams from ducts or stacks,
- Measurement of particulate mass loading and size distribution,
- Collection of organic species for subsequent analysis, and
- Collection of vaporous trace elements for subsequent analysis

In addition to these functional requirements, the SASS train must be portable, corrosion resistant, easily cleanable, reliable, and accurate.

Included in this paper will be a review of the SASS design philosophy, followed by a brief description of the individual components of the SASS train, a review of tradeoffs and alternate configurations considered during conceptual design, a description of cyclone calibration methods and their results, and a list of suggested modifications and improvements to the SASS. These topics, and others, are covered in greater detail in Reference 3.

The SASS design and development program was sponsored by the Industrial Environmental Research Laboratory (RTP) of the U. S. Environmental Protection Agency. Project Officer for the program was Mr. William B. Kuykendal of the Process Measurements Branch; his support and guidance are gratefully acknowledged.

Design Philosophy

At the start of the SASS development program, Level 1 procedures had not yet been established, and the function of the SASS not fully defined. The basic SASS design philosophy was established at a meeting at Acurex in March, 1976. Attending were representatives of Acurex, EPA, and TRW, Inc. Figure 1 shows the design schematic determined at that meeting for the complete SASS train. This basic design concept has been adhered to throughout the course of the SASS development program.

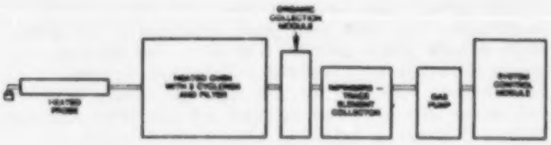

ORGANIC COLLECTION MODULE
HEATED PROBE
HEATED OVEN WITH 3 CYCLONES AND FILTER
IMPINGER — TRACE ELEMENT COLLECTION
GAS PUMP
SYSTEM CONTROL MODULE

Figure 1. Design schematic — SASS train.

In addition to establishing the design philosophy, at the beginning of the development program the EPA suggested guidelines for the detailed design phase. These included:

1. The cost of the completed SASS train was to be kept as low as possible. A target figure of $17,000 for a barebones, but complete, SASS train was suggested. An additional cost of not more than $3,000 was allowable for an automatic control feature in the event that such a feature was judged desirable.

2. The SASS design was to be made as interchangeable as possible with the High Volume Stack Sampler (HVSS). This was felt to be desirable because many of the potential users of the SASS train already owned an HVSS. In some cases it might be possible to upgrade an HVSS to a SASS, cutting costs considerably to users.

3. Cyclones, rather than a stage impactor, were specified as the method for determining particulate size distribution. The primary reasons for choosing cyclones was the desire to collect large particulate samples (~1 gram) for subsequent chemical and biological analysis, and the requirement for trouble-free field use.

It was considered necessary to maintain a constant sampling flowrate through the cyclone assembly, since cyclone collection efficiency varies with gas flowrate.

4. The probe and oven were to be heated to eliminate the possiblity of water, acid, or organics condensing.

5. The organic sorbent material in the organic module was to be held at 20°C.

6. A flowrate of 0.00189 m^3/sec (4.0 scfm) was to be maintained at the cyclones.

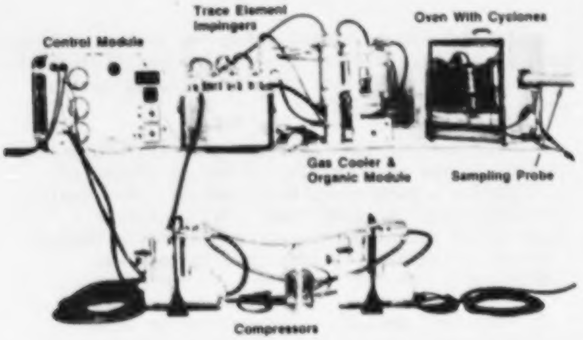
7. The only acceptable materials of construction for the SASS parts that would contact the sample stream were to be Type 316 stainless steel, fully fluorinated Teflon, or Pyrex glass.

8. The SASS was to be designed for ease of sample recovery and post-test cleanup.

The design of the SASS as ultimately constructed reflects our best solution to these conflicting requirements.

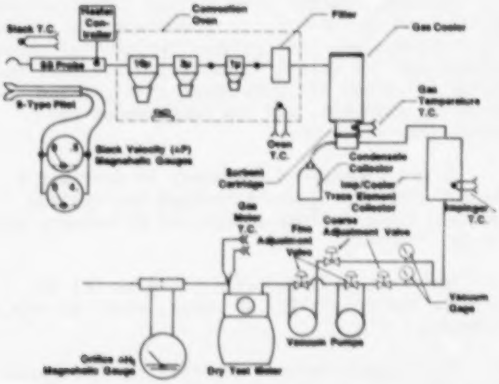
SASS Design and Construction

The complete SASS train is shown in Figure 2. A few basic components of the train such as the heated probe, the vacuum pumps, and the control module are the same ones used previously for the High Volume Stack Sampler (HVSS). The heated cyclone-filter particulate collection system, the organic module, and the impinger/trace element collector are original designs of the SASS program. Figure 3 shows a detailed schematic diagram of the Source Assessment Sampling System as constructed.



Trace Element Impingers
Oven With Cyclones
Control Module
Gas Cooler & Organic Module
Sampling Probe
Compressors

Figure 2. Source Assessment Sampling System (SASS).



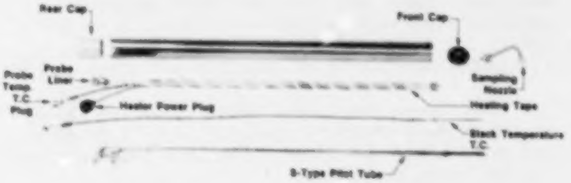
Stack T.C.
Heater Controller
Convection Oven
Filter
Gas Cooler
SS Probe
10µ
3µ
1µ
S-Type Pitot
Oven T.C.
Gas Temperature T.C.
Stack Velocity (ΔP) Magnehelic Gauges
Sorbent Cartridge
Condensate Collector
Imp/Cooler Trace Element Collector
Impinger T.C.
Gas Meter T.C.
Fine Adjustment Valve
Coarse Adjustment Valve
Vacuum Gage
Vacuum Pumps
Orifice ΔH Magnehelic Gauge
Dry Test Meter

Figure 3. Schematic of SASS.

Heated Probe

The SASS probe extracts gas/particulate samples from the source being tested, monitors the temperature and gas velocity of the source, and maintains sample temperatures above the condensation point of water/SO_3 mixtures.

Some important features of the probe (shown disassembled in Figure 4) are the Type 316 stainless steel sampling tube; the fiberglass-insulated strip heater wrapped around the sampling tube; a round probe body to allow sealing of the sampling port and rotation of the probe as necessary; strain relief for all electrical, thermocouple, and pilot line connections; a calibrated S-type pitot tube; and easily interchangeable probe tips with available diameters from 0.64 cm (1/4 in) to 1.92 cm (3/4 in) in 0.16-cm (1/16-in) increments. The standard probes come in lengths of 3, 5 and 10 feet and are designed to withstand duct temperatures of 330°C.



Rear Cap
Front Cap
Probe Temp T.C. Plug
Probe Liner
Heater Power Plug
Sampling Nozzle
Heating Tape
Stack Temperature T.C.
S-Type Pitot Tube

Figure 4. Probe

A stainless steel liner is used in the standard probe rather than a glass liner for two reasons. First, the durability of the metal liner is much greater than a glass liner. And second, even though glass is much more resistant to corrosion, there is so much stainless steel in the cyclones, filter, and organic module that the small additional amount in the probe was felt to be unimportant.

Particulate Collection System

The purpose of the particulate collection system is to maintain the sample gas stream at 205°C while collecting the particulate in three cyclones and a backup absolute filter. Figure 5 shows the three cyclones and the filter holder inside the cyclone oven.

The nominal cut sizes of the three cyclones are 10, 3, and 1 µm respectively. Together with the fiber glass backup filter, the system separates particulate fraction of the sample into four nominal size ranges:

- > 10 µm
- 3 to 10 µm
- 1 to 3 µm
- < 1 µm

The design of the small and middle cyclones (1 and 3 µm) were based on Southern Research Institute designs that predated the SASS development program. Applying standard cyclone design equations to the 10-µm cyclone results in a collector 75 cm high by 20 cm in diameter, which is far too large for portable, lightweight sampling equipment. Professor Andrew McFarlane and one of his students (1), had developed a design procedure for smaller "stub" cyclones; his methods were adapted to reduce the cyclone size. This type of cyclone

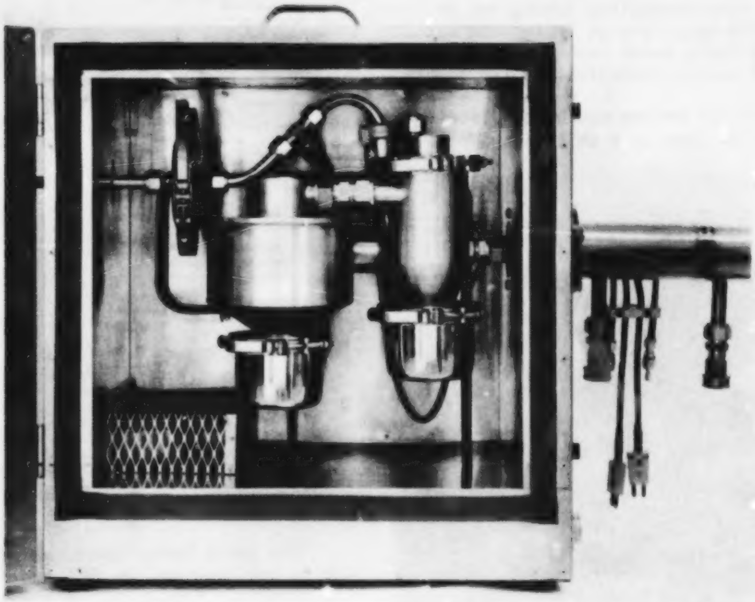
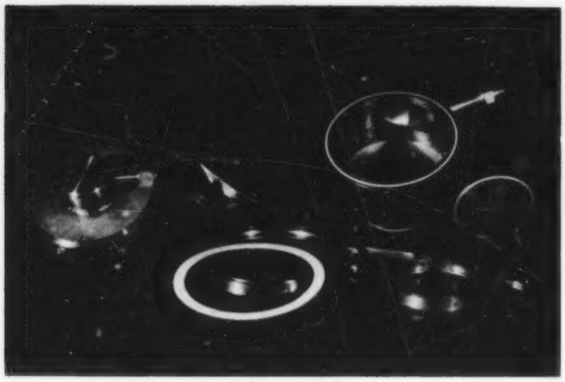


Figure 5. Cyclones and oven.

can be much smaller because it uses internal vanes to destroy interior vortices. Figure 6 shows an exploded view of the 10-μm cyclones. Note the "vortex breakers" -- the crossed metal pieces -- in the collection cup and in the outlet tube. Efficiency is reduced with the stub cyclone design. For the SASS application the reduced efficiency was felt to be tolerable, since the large cyclone serves only as a scalping device.

The bodies of all three cyclones are spun 316 stainless steel to accommodate both the lightweight and strength requirements. Top and bottom flanges and inlet and outlet tubes are machined and welded to the spun bodies.

Close packing of the cyclones and filter system is essential for small size and light weight. However, the particulate collection system must also



10μ cyclone (disassembled)

Figure 6. Large (10 μm) cyclone breakdown.

be easy to assemble and disassemble since the system is completely broken down for sample recovery after each test. Short interconnecting tubing and no sharp bends are also necessary as tubing can act as a collector and sharp bends can cause erosion, damaging the train and/or contaminating the sample.

The cyclone-filter system can be completely assembled outside the oven as a unit as shown in Figure 7.

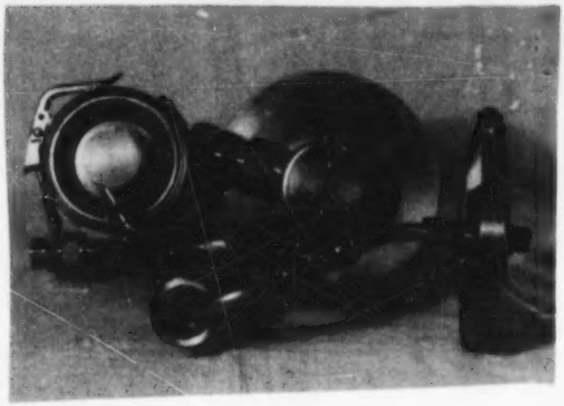


Figure 7. Cyclones — top view.

The oven provides a constant temperature environment and mechanical protection for the cyclones and filter. It also supports the probe by means of a collar attached to its side.

Organic Module

The sample gas leaves the filter holder at 205°C, cleaned of particulate but still containing organic and trace element vapors. The organic module (Figure 8) cools the gas stream and directs the cooled gas and any condensate through an adsorbent bed. The bed will collect most organic species of molecular weight greater than about C_6, as well as some fraction of the metallic trace elements present. The condensate is collected and the cool gas passes to the impingers.

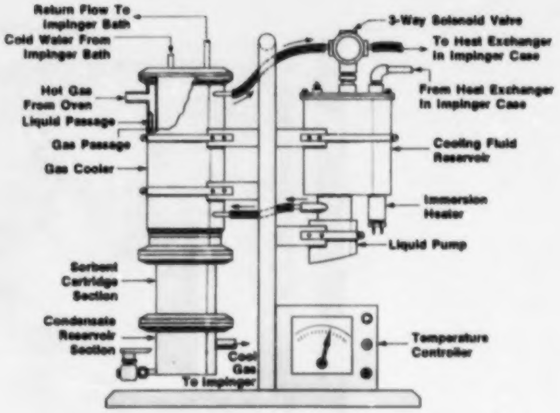

Return Flow To Impinger Bath
Cold Water From Impinger Bath
Hot Gas From Oven
Liquid Passage
Gas Passage
Gas Cooler
Sorbent Cartridge Section
Condensate Reservoir Section
Cool Gas To Impinger
3-Way Solenoid Valve
To Heat Exchanger In Impinger Case
From Heat Exchanger In Impinger Case
Cooling Fluid Reservoir
Immersion Heater
Liquid Pump
Temperature Controller

Figure 8. Organic module schematic.

The two primary functions of the organic module are to cool the gas to 20°C and collect organics on the sorbent. From a design viewpoint, gas cooling is the more difficult task. The cooler must remove about 1 kW of heat from the gas, requiring a considerable amount of heat transfer surface. The cooler must also be lightweight, durable, free of plugging, and easy to clean and recover the sample.

Three separate conceptual cooler designs were considered: an externally-cooled coil, a parallel tube heat exchanger (with the sample gas passing down the inside of the tubes and cooling fluid outside), and a thin film heat exchanger in which a thin film of sample gas passes between cooled walls. As each design was considered in detail, it became clear that the two most difficult constraints were the requirement to cool the gas from 205°C to 20°C and still retain easy disassembly, cleaning, and reassembly. These constraints favored a design with a large surface area composed of smooth, easily accessed surfaces. The thin film heat exchanger concept was judged clearly superior in these areas. This cooler could be made from metal or glass, although metal was chosen for its durability. Figure 9 schematically shows each of the gas cooler concepts, and Table 1 lists the advantages and disadvantages of each.

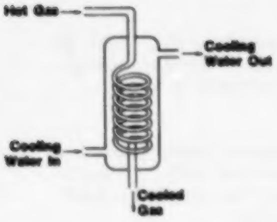

Hot Gas
Cooling Water Out
Cooling Water In
Cooled Gas

Figure 9a. Coiled-tube cooler.

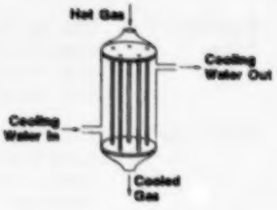

Hot Gas
Cooling Water Out
Cooling Water In
Cooled Gas

Figure 9b. Straight-tube cooler

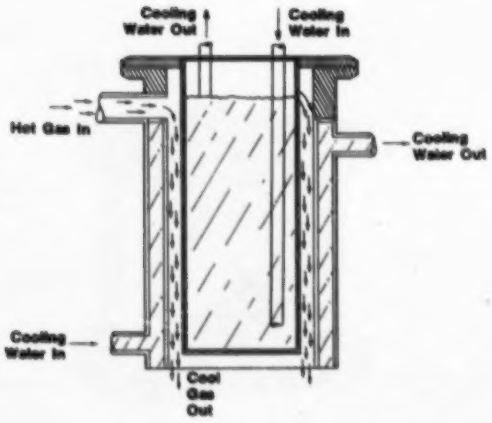

Cooling Water Out
Cooling Water In
Hot Gas In
Cooling Water Out
Cooling Water In
Cool Gas Out

Figure 9c. Thin film cooler.

TABLE 1. COMPARISON OF GAS COOLER CONCEPTS

Design	Advantages	Disadvantages
Coil	Easy to construct. Relatively inexpensive. Low gas pressure drop. Capable of adequate cooling with metallic construction, but not glass.	Very difficult to clean. Must be large and bulky to achieve necessary heat transistor.
Parallel Tubes	Low gas pressure drop. Capable of adequate cooling with metallic construction, but not with glass. Compact.	Moderately difficult to clean. Complex design. Relatively costly.
Thin Film	Cleaning very easy. All surfaces accessible. Low pressure drop. Small, compact. Capable of adequate cooling with either metallic or glass construction.	Somewhat more expensive than the coil. Cheaper than the parallel tube design.

Precise temperature control of the sorbent bed is essential for reproducible organic species collections. Accordingly, the organic module temperature control system is designed to maintain the sample gas temperature just upstream of the sorbent cartridge at any temperature between 15°C and 80°C. (For Level 1 sampling, 20°C is the required setpoint.)

As the sample gas is cooled, water, acid, and heavy organics will usually condense. The organic module is designed so that the cooled gas leaving the gas cooler section, along with any liquid condensation formed, passes through the sorbent bed. The sorbent is typically a porous polymer gas chromatographic bed packing material. The sorbent is held within the sorbent cartridge (Figure 10) by 80-mesh Type 316 stainless steel screens. The cartridge is designed to be easily removed and replaced with an identical clean cartridge when several SASS tests are to be made sequentially.

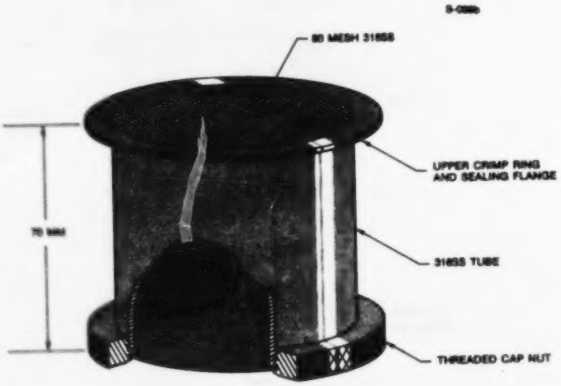
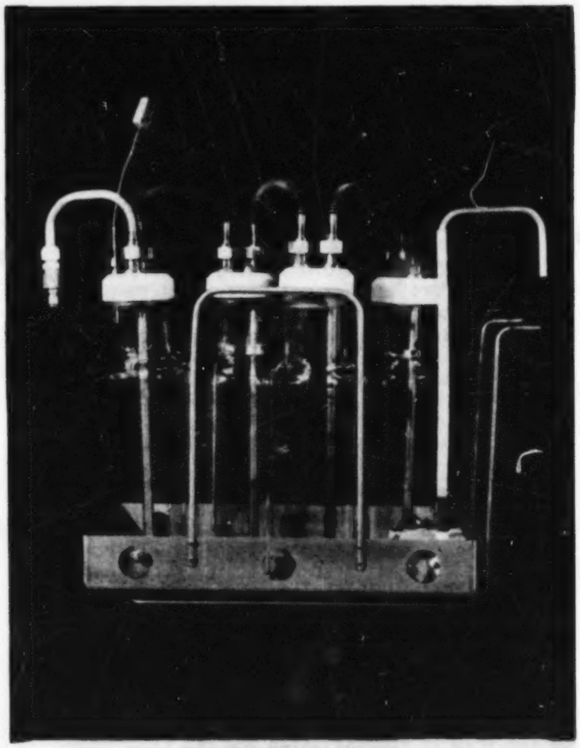


Figure 10. Sorbent cartridge.

After the gas and condensate exit the sorbent cartridge, they pass into the condensate reservoir section, where the condensate collects and is periodically pumped to a storage bottle. The gas exits a tube at the top of the condensate reservoir section and passes to the impinger/trace element assembly.

Impinger Assembly

The impinger assembly (Figure 11) collects any remaining trace elements for subsequent analysis, and dries the sample gas stream to avoid damaging the gas pumps and flow monitoring instrumentation. Four heavy-wall glass bottles contain chemical solutions or moisture sorbent. The first impinger bottle contains an oxidation solution of hydrogen peroxide to collect sulfur oxides. The next two bottles contain a solution of 0.2 molar ammonium persulfate with 0.2 molar silver nitrate to collect trace elements. In each of these three liquid-containing bottles, a straight section of tubing ducts the sample gas below the liquid levels. The sample gas bubbles through the liquid, allowing the various pollutant species to be scrubbed out. The fourth impinger bottle contains granular silica gel to dry out the gas.



Impinger train out of case

Figure 11. Impinger assembly.

The standard HVSS four-bottle impinger train provides the basis for the SASS impinger design, with one important modification. Because of the relatively high-pressure drop in several of the SASS components, the impinger assembly operates at a substantial vacuum (10 to 20 inches Hg). The actual volumetric flowrate in the impingers is as high as 0.0057 m^3/sec (12 acfm), leading to excessive splashing of the impinger solutions and possible solution carryover. In order to eliminate this problem, special oversized glass impinger bottles are used.

Vacuum Pumps

Two vacuum pumps connected in parallel are used with the SASS. These carbon vane-type pumps are modified with a special shaft seal to reduce the leak rate to better than Method 5 standards. Only one of the 3/4-hp pumps is necessary to draw the 4.0 scfm of sample gas through a clean train, but once the filter begins to accumulate particulate, a second pump is needed to make up for the additional pressure drop.

Control Unit

The control unit contains all of the instruments for measuring stack velocity, sampling flowrate and cumulative flow, and temperatures of various points in the sampling system. The unit is identical to that of the Method 5 train and its controls and data readouts are identified in Figure 12.

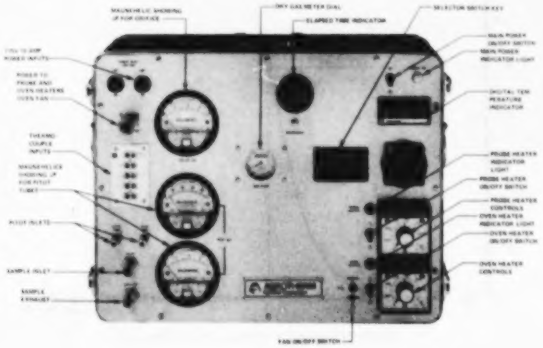

MAGNEHELIC SHOWING ΔP FOR ORIFICE
DRY GAS METER DIAL
ELAPSED TIME INDICATOR
SELECTOR SWITCH KEY
115V 15 AMP POWER INPUTS
MAIN POWER ON/OFF SWITCH
MAIN POWER INDICATOR LIGHT
POWER TO PROBE AND OVEN HEATERS OVEN FAN
DIGITAL TEMPERATURE INDICATOR
THERMOCOUPLE INPUTS
MAGNEHELICS SHOWING ΔP FOR PITOT TUBE
PROBE HEATER INDICATOR LIGHT
PROBE HEATER ON/OFF SWITCH
PROBE HEATER CONTROLS
OVEN HEATER INDICATOR LIGHT
OVEN HEATER ON/OFF SWITCH
PITOT INLETS
SAMPLE INLET
OVEN HEATER CONTROLS
SAMPLE EXHAUST
FAN ON/OFF SWITCH

Figure 12. Control unit.

SASS Cyclone Calibration

The characterization of the SASS cyclones has been underway almost continuously since the completion of the first SASS prototype. Initial efforts were conducted by Southern Research Institute using a Vibrating Orifice Aerosol Generator. Later calibration tests were performed at Acurex using a different method involving dispersion in air of polydisperse aluminum spheres. All tests were done at normal cyclone operating conditions (0.00189 m^3/sec [4.0 scfm] and 205°C [400°F]). At the time of writing, results have been obtained with both methods that are reasonably consistant and are believed to represent the actual performance of the cyclones.

The object of the various cyclone calibration tasks ultimately is to determine the cyclone efficiency curve; from the curve can be obtained a commonly used figure-of-merit for the cyclone called the D_{50} cut diameter. Figure 13 illustrates these concepts. The efficiency of particle collection is plotted against the particle diameter. For each particle diameter, therefore, the effectiveness of the cyclone is determined. For example, Figure 13 shows that for this particular (fictitious) device, if a large number of 2.5-µm diameter particles are introduced, 17.5 percent will be collected and 82.5 percent will pass through uncollected. The particle diameter at which half of the particles are collected is the D_{50} cut diameter; Figure 13 shows the D_{50} cut diameter of that device to be 3.0 µm. The D_{50} cut diameter, often abbreviated to "cut size" is commonly used as a rough indication of the collection cutoff of a cyclone.

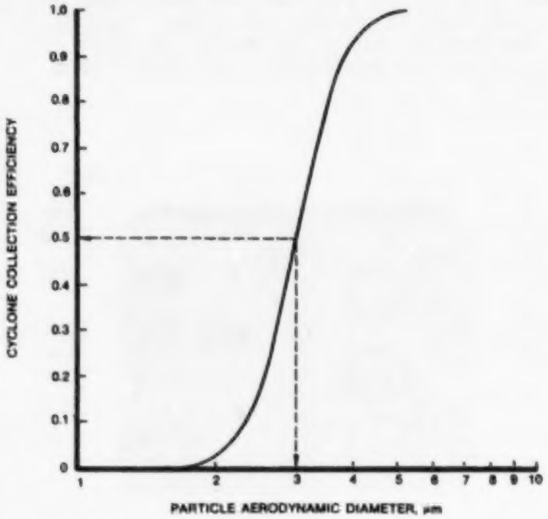


Figure 13. Typical cyclone fractional efficiency curve.

Note that Figure 13 expresses particle diameters as aerodynamic particle diameters. It is important to distinguish aerodynamic diameters from physical diameters. The physical diameter is the dimension of the particle obtained by physical measurement, for example with a microscope and reticle. For nonsymmetrical particles, the physical diameter of a given particle may have several different values, depending on the measurement axis chosen. The aerodynamic diameter (sometimes called the Stokes diameter) is defined as the diameter of the equivalent spherical particle of unit specific gravity having the same terminal settling velocity as the particle in question. The advantages of using the aerodynamic diameter to characterize the particles used for cyclone calibration are twofold. First, each particle is uniquely characterized, independent of any choice of physical dimension. Second, and most important, since the basic cyclone separation mechanism depends on Stoke's law, measuring particle diameter in terms of Stoke's law, behavior assures that calibration data will be valid over wide ranges of particle size, shape, and density.

Cyclone Calibration Tests With Monodisperse Aerosol

The Southern Research Institute calibration efforts which used monodisperse particles, occurred in two phases. Initial calibrations were made at room temperature, wtih the intent of calculating cyclone D_{50} cut diameters at 400°F by use of accepted design equations. Based on these intial calculated values, modifications were made to the SASS cyclones to shift their cut points closer to the 1, 3, and 10 µm values desired. It was discovered subsequently that the design equation used to adjust the cyclone D_{50}'s to 400°F was inapplicable to small cyclones such as the SASS. The second phase of calibrations at SoRI involved actual calibrations at 400°F. These efforts resulted in calibration data (for the middle cyclone only) that are believed to be accurate.

The same basic procedure has been used in all of the SoRI calibration work. The following description of their experimental procedure is drawn from Reference 2.

The SASS train cyclones were calibrated using a Vibrating Orifice Aerosol Generator (VOAG). The VOAG generates monodisperse (all particles the same size) dye particles of ammonium fluorescein or Fast Turquoise 8 GLP dye. The VOAG used in this study was designed and built at Southern Research Institute. However, similar devices have been reported by several authors previously, and a commercial unit is available from Thermo Systems, Inc.

Using VOAG, cyclone efficiency can be determined as follows. Monodisperse aerosol of a certain particle size, generated by the VOAG, is fed into the cyclone to be calibrated. Some of the aerosol will be collected in the cyclone and some will pass through and be collected on a backup filter. The mass ratio of particulate collected by the cyclone divided by the total aerosol fed to the cyclone defines the efficiency of the cyclone at that particle size. The size of the particles generated by the VOAG is then adjusted and the experiment repeated. After a number of iterations, a complete fractional efficiency curve results.

Figure 14 is a schematic diagram showing the operating principle of the VOAG. The dye is fed through a vibrating orifice were it is atomized and mixed with air in the drying chamber. The particle size is controlled by the frequency at which the orifice is being vibrated and the concentration of the dye solution. As the particle stream leaves the drying chamber, it passes through a charge neutralizer to reduce agglomeration and loss of particles due to electrostatic forces.

The advantage of the monodisperse calibration method is the direct measure of collection efficiency of the cyclone versus particle size. The chief drawback is that the cyclones experience very low mass loadings, many orders of magnitude lower than field conditions.

Table 2 summarizes Southern Research Institute's calibration of the middle cyclone. Data are shown both with and without the vortex breakers (Figure 6) in place. Note that the aerodynamic cut diameter of the middle cyclone is closer to the desired value of 3 μm when the vortex breaker is absent. The collection efficiency curves for these tests are shown in Figure 15. Note that in Figure 15 the data are plotted using physical diameter, rather than aerodynamic diameter.

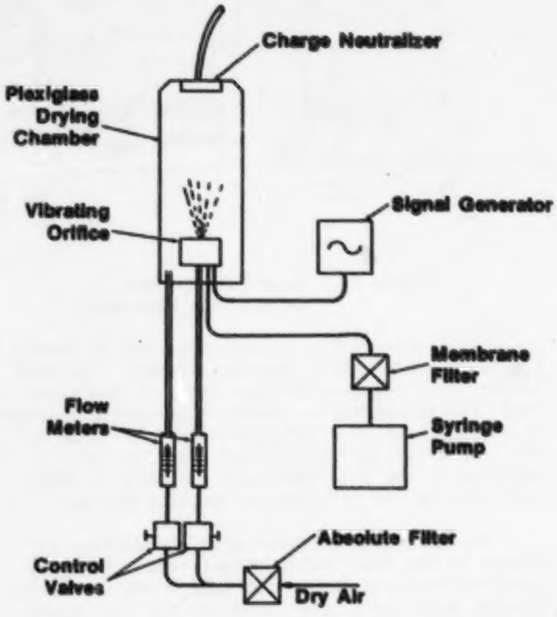


Figure 14. Schematic representation of the Vibrating Orifice Aerosol Generator.

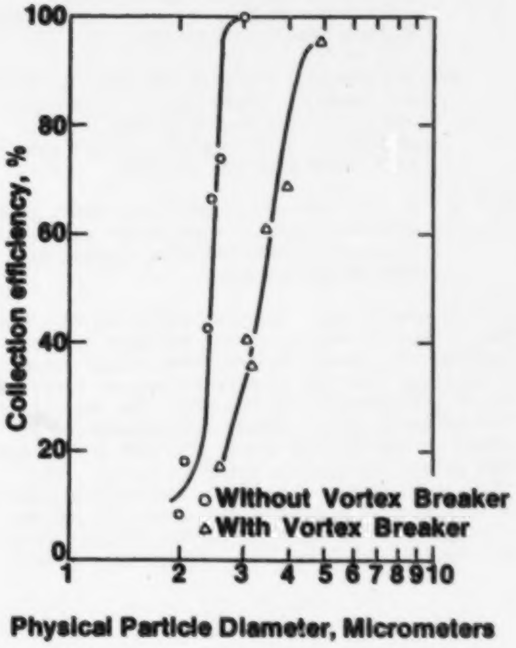


Figure 15. SASS middle cyclone efficiency curves.

TABLE 2. SUMMARY OF SORI CALIBRATIONS OF MIDDLE CYCLONE

Material	Vortex Breaker	Temperature	Flowrate ft^3/min Actual/Standard	D_{50} Physical Micrometers	D_{50} Aerodynamic Micrometers
Turquoise Dye	OUT	400°F	6.50/4.00	2.5	3.5
Turquoise Dye	IN	400°F	6.50/4.00	3.4	4.9

Cyclone Calibration Tests With Polydisperse Aerosol

The Acurex SASS cyclone calibration test series was conducted by an entirely different method than was used by SoRI. The Acurex method involves the dispersion of polydisperse (particles of varying diameters) particles, at concentrations more representative of actual field conditions. It was desirable to do a second series of calibration tests for several reasons:

- A separate series of calibrations using a different method would -- if the results agreed -- greatly increase confidence in the correctness of the calibrations
- The extremely low particle mass concentrations with the monodisperse (SoRI) calibration method required confirmation at more realistic loadings
- The physical state of the SoRI dye particles was unknown. There was a feeling that any stickiness caused by hydroscopic absorption or incomplete solvent evaporation might bias the results.
- At the time the polydisperse tests began, problems with the SoRI method at elevated temperature made ultimate success with that method uncertain

Figure 16 shows the test apparatus in schematic form. Metered amounts of air and test dust are combined in a powder feeder. The powder feeder is so designed that the dust particles are deagglomerated and suspended in the air. The dust cloud then enters a heater, where its temperature is raised to the desired level. The hot dust cloud then enters the cyclone being evaluated. Each particle is either captured by the cyclone (ending up in the cyclone cup) or exits the cyclone and is captured on an absolute backup filter. Clean air is exhausted from the filter holder to the room.

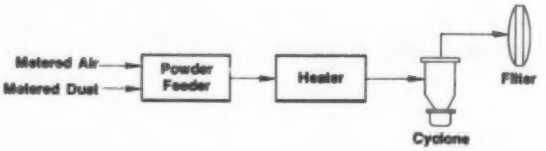


Figure 16. Polydisperse cyclone calibration apparatus schematic.

Figure 17 shows the apparatus in more detail. Compressed air is filtered, regulated, and then passed through a square-edged critical flow orifice. The flowrate through this type of orifice depends only on upstream pressure, so long as the temperature remains constant and the downstream absolute pressure is less than about half of the upstream pressure. In the calibration apparatus these conditions are easily met, so a constant volumetric flowrate of 0.00189 m^3/sec (4.0 scfm) was held simply by maintaining a constant reading on the upstream pressure gauge.

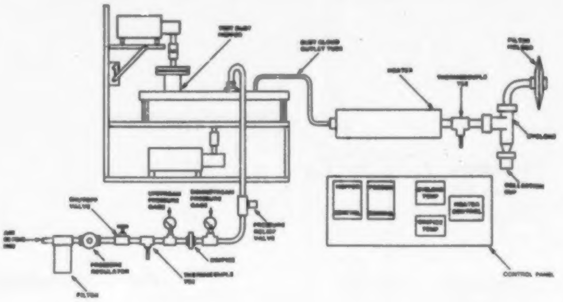


Figure 17. Detail of cyclone calibration apparatus.

The carrier air -- clean, dry, and at constant flowrate -- now enters the dust feeder. The dust feeder is of the grooved-disc type, in which the test dust is metered by means of pneumatic unloading of a groove cut in a rotating disc. The size of the (powder-filled) groove and the speed of rotation of the disc determine the rate at which test dust is fed into the calibration system.

The test dust is mixed with the metered air stream in the dust feeder outlet tube. The dust cloud velocity in the outlet tube is deliberately held at near sonic conditions in order to assure maximum dispersion of the dust particles. At the point the outlet tube enters the heater, a step enlargement in the diameter of the tube reduces the gas velocity through the heater to about 120 m/sec. The heater itself is a stainless steel tube wrapped with a heating tape. The wall temperature of the tube is maintained at about 330°C, allowing the dust cloud to reach 205°C by the time it exits the 0.5-meter long heater. Feedback temperature control of the exit cloud temperature is maintained by a thermocouple and temperature controller.

The cyclone being calibrated is attached to the outlet of the heater, and is wrapped with thermal insulation during calibration tests so the 205°C operating temperature is maintained. A standard SASS filter holder supports a glass fiber absolute filter.

For the polydisperse aerosol calibration tests, an aluminum powder with a size range from 1 µm to 25 µm and a mass median diameter of 6 µm was used. The data reduction method requires measurement of the size distribution and quantity of dust collected in both the cyclone dust cup and on the filter. Coulter counter measurement was chosen for determining the distribution, since for the particle sizes of interest it was known to give reliable and reproducible results.

From this information a simple material balance on each differential element of particle size allows reconstruction of the distribution of the test dust entering the cyclone, no matter how it may have been changed during passage through the dust feeder and heater. This method of analysis was used for all of the cyclone calibrations reported here. Details of the data reduction method are included in Reference 3.

Two complete sets of SASS cyclones were calibrated using the polydisperse method. Each set consisted of three cyclones -- one small, one medium, and one large. The first set calibrated was a part of an EPA-owned SASS train. The large and medium cyclones were calibrated both with and without their swirl breakers; thus a total of five complete cyclone calibrations were obtained. Figures 18 and 19 show scanning electron photomicrographs of the test dust and representative samples of dust collected by the cyclones. The spheroidal nature of the particles can be seen.

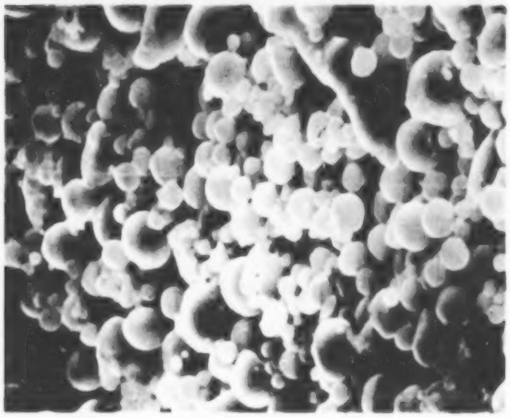


Figure 18. Aluminum test dust.

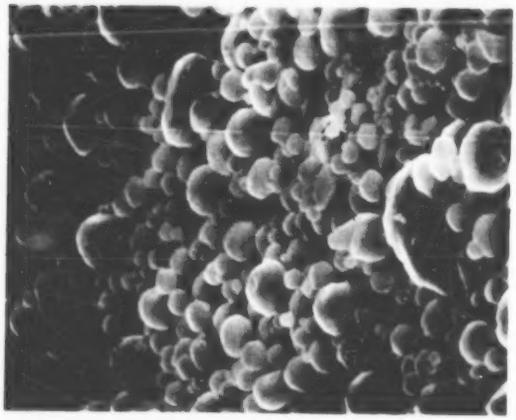


Figure 19a. Small cyclone catch.

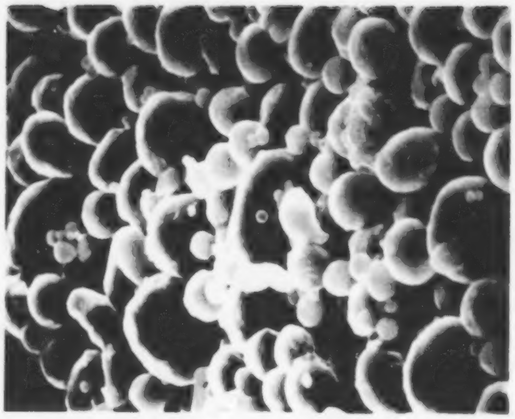


Figure 19b. Large cyclone catch.

Figure 20 shows the calibration results for the first set of SASS cyclones. Table 3 shows the D_{50} cut diameters for each of the five cyclone configurations expressed as both physical and aerodynamic diameters. The SoRI D_{50} values for medium cyclone are shown for comparison. The agreement between the two methods is good.

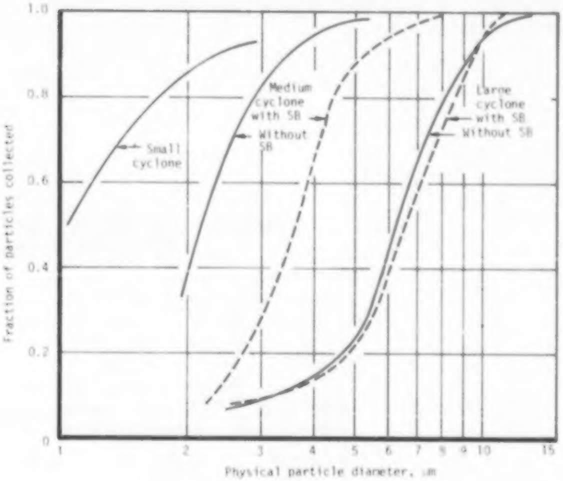


Figure 20. Physical particle diameter, μm.

TABLE 3. SUMMARY OF CALIBRATION RESULTS

Cyclone	Cyclone D_{50} Cut Diameter, µm		
	Aerotherm		SoRI
	Physical	Aerodynamic	Aerodynamic
Large (with SB)	6.6	10.8	
Large (w/o SB)	6.2	10.2	
Medium (with SB)	3.65	6.0	4.9
Medium (w/o SB)	2.18	3.6	3.5
Small	1.05	1.55	

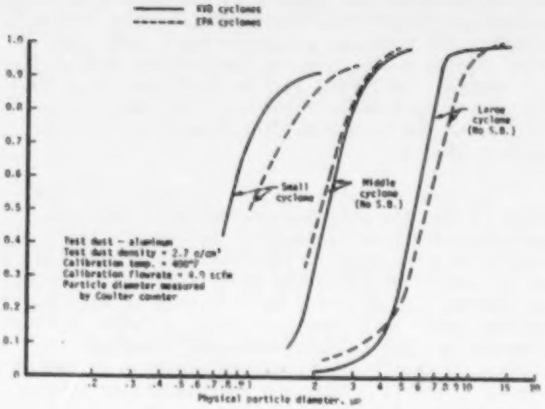


Figure 21. SASS cyclone calibration data.

A second set of SASS cyclones has recently been calibrated by this method. The cyclones tested are a part of a SASS train owned by KVB, Inc. These cyclones were calibrated with the swirl breakers removed from the large and middle cyclones. Figure 21 compares the calibration results for the KVB and EPA SASS cyclones. The two cyclone sets compare quite well for the large and medium cyclones, and reasonably well for the small cyclone. This is to be expected, as all of the uncertainty factors in the calibration method -- particle deagglomeration, Coulter counter accuracy, particle shape uniformity -- are more significant for the smaller particle sizes.

Table 4 shows the physical and aerodynamic D_{50} cut diameters of the KVB and EPA cyclones. The D_{50} aerodynamic cut diameter of the two SASS cyclone sets calibrated to date are reasonably close -- averaging 9.7, 3.7, and 1.5 µm -- to the desired cut diameters of 10, 3, and 1 µm that were established at the start of the SASS development program.

TABLE 4. COMPARISON - KVB AND EPA SASS CYCLONES, AEROTHERM CALIBRATION METHOD

	D_{50} Cut Diameters, µm			
	KVB		EPA	
Cyclone	Physical	Aerodynamic	Physical	Aerodynamic
Large[a]	5.61	9.2	6.20	10.2
Medium[a]	2.30	3.8	2.18	3.6
Small	0.81	1.3	1.05	1.7

[a] Swirl busters removed

SASS Modifications and Improvements

As with any complex instrument, field use has demonstrated the need for changes to the SASS. Some changes have been accomplished, and some have been recommended and are being studied. Some of these recommended changes being studied are discussed here.

Table 5 lists SASS improvements and modifications that have been suggested by a number of SASS users as a result of testing occurring during the past year. Most of the suggested modifications are self explanatory; an exception is the concept of adding isokinetic sampling capability to the SASS.

TABLE 5. SUGGESTED SASS MODIFICATIONS

Type of Improvement	Suggested Change
Corrosion Resistance	• Precious metal plating of the sample-contacted parts of the organic module • Fully concentric organic module gas cooler • All glass/Teflon organic module
Convenience	• Jig for out-of-oven cyclone assembly • Index marks on cyclones • Ball-and-socket fitting for filter holder • Increase impinger case size. Insulate. • Add drain cock to impinger case • Check valves in impinger tubes • Replace ice with mechanical refrigeration system
Durability	• Increase cyclone wall thickness • Tapering inlet to filter holder to eliminate filter erosion by reducing gas velocity • Heavier cyclone collection cups • Less fragile condensate collection bottle and adaptor
Improved Accuracy	• Add isokinetic sampling capability to the SASS

It may be desirable for some (as yet undefined) Level 2 or Level 3 procedures to improve the accuracy of particulate size distribution measurements. Isokinetic sampling at the nozzle would provide for this improved accuracy; however, isokinetic sampling is not possible with the present SASS train because of the requirements for constant gas flowrate through the cyclones. Figure 22 shows one way of adding isokinetic sampling capability to the SASS, while continuing to operate the cyclones at a constant flowrate.

The SASS train would be basically unchanged from its original configuration, except for the addition of the recycle loop. Isokinetic sampling would be achieved by first choosing a nozzle size such that at 0.00189 m^3/sec (4.0 scfm) through the nozzle, and for the maximum stack gas velocity expected during the test, stack gas and nozzle velocities are matched. The probe would then be inserted into the stack, and the pitot reading used to set the control-module flowrate at a value that gives isokinetic sampling at the nozzle. This flowrate will in general be less than 4.0 scfm, and will vary as the stack gas velocity varies. Throughout the duration of the test, the flowrate through the train (as measured at the control module) will be changed frequently to reflect changes in stack gas velocity, temperature, or pressure.

The purpose of the recycle loop shown on Figure 22 is to automatically maintain a constant 4.0-scfm flowrate at the cyclones while the train flowrate varies. The small cyclone is used as differential pressure flowmeter. A gas pump moves the recycle gas stream from the low-pressure point after the filter to the high-pressure point upstream of the first cyclone. The recycle loop is fully automatic in that any deviation from a flowrate of 4.0 scfm at the small cyclone immediately actuates the recycle stream valve to correct the flowrate to that value.

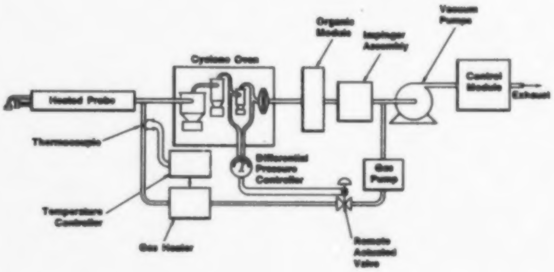


Figure 22. Isokinetic SASS.

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2. Cushing, K. M. et. al., "Particulate Sampling Support: 1977 Annual Report," EPA-600/7-78-009, January 1978.

3. Blake, D. E., "Source Assessment Sampling System-Design and Development," EPA-600/7-78-018, February 1978.

FIELD EVALUATION OF THE SASS TRAIN AND LEVEL-1 PROCEDURES

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This paper presents the results of a two-phased evaluation of Level-1 environmental assessment procedures. Phase I was a field evaluation of the SASS train. Three sample runs were made with two SASS trains sampling simultaneously and from approximately the same sampling point. A Method-5 train was used to estimate the "true" particulate loading. Comparisons of the SASS trains are made for total particulate, particle size distribution, organic classes, and trace elements. Phase II consisted of providing three participating organizations with control samples to challenge the spectrum of Level-1 analytical procedures. Estimates of intra- and interlaboratory precision are made.

Introduction

An experimental program designed to evaluate the source assessment sampling system (SASS) and the associated Level-1 analytical procedures has been completed. The project was conducted in two phases. Phase I consisted of a field evaluation of the SASS involving simultaneous sampling with two SASS trains and a Method-5 train. Results of Phase I are used to estimate within and between train precisions for particulate, organic, and inorganic sampling, and to estimate the biases of the SASS trains with respect to Method 5 for total particulate determinations. Phase II consisted of an interlaboratory evaluation of the analytical methods involving the analysis of split samples by participating laboratories.

The Research Triangle Institute (RTI) coordinated the experimental program with Arthur D. Little (ADL), Southern Research Institute (SoRI), TRW, and Radian Corporation. ADL analyzed all the field samples collected in Phase I of the program and prepared and analyzed the control samples used in Phase II of the program. SoRI and TRW each provided a field crew and a SASS train for Phase I and participated in Phase II by analyzing the control samples provided by ADL. Radian Corporation provided a field crew and a Method-5 train for Phase I and participated in Phase II by analyzing the control samples.

As stated above, the objectives of this project were; (a) to evaluate the SASS, and (b) to evaluate the analytical procedures. Assessment of field crew and/or analyst performance was not a program objective. Actions taken to eliminate or minimize extraneous sources of variability in the field evaluation of the SASS included the following:

a. Each participating organization was requested to provide a crew experienced in the operation and field use of SASS.

b. Field crews were briefed on and directed to use the approved and documented Level-1 sampling procedures.[1]

c. RTI provided on-site coordination of the field sampling activities.

d. Calibration checks were made on the volume measurement systems (dry gas meters) of the SASS trains and on the gas velocity measurement systems of the two SASS trains and the Method-5 train.

e. All field samples were analyzed by one organization (i.e., ADL), eliminating the between laboratory component of variability of the analytical methods.

In an effort to minimize analyst/laboratory biases in Phase II of the program, RTI personnel visited each organization to discuss the analytical procedures and to review the laboratory facilities and apparatus to be used in the analysis of the control samples. Also, as RTI analyzed the data for the final report, outliers or suspicious data were brought to the attention of the reporting organization for verification and/or correction as appropriate.

A description of the test plan for the field evaluation of the SASS and for the interlaboratory evaluation of the analytical procedures is given in Section 2. Results of the field evaluation of the SASS are presented and discussed in Section 3. The interlaboratory evaluation of the analytical procedures is described in Section 4. A brief summary and interpretation of the results of both phases of the program are contained in Section 5 of this paper.

Discussion of Experimental Test Plan

Procedures for Level-1 environmental assessments for both sample collection and sample analyses have been specified by the Process Measurements Branch (PMB) of the Industrial Environmental Research Laboratory (IERL).[1] In order for the Level-1 procedures to be effective, the precision and accuracy of both the sample collection and sample analysis phases of the measurement process must be sufficient to satisfy Level-1 data quality requirements.

The primary procedure for characterizing gaseous process streams in environmental assessments is to use the SASS for sample collection and specified analytical methods for subsequent sample analysis. The SASS and some of the analytical methods, at least for this application, are still in the developmental stage to the extent that prior to this study they had not been subjected to collaborative (or interlaboratory) tests. The purposes of this project were to evaluate the SASS under field conditions (Phase I) and to conduct an interlaboratory evaluation of the associated analytical methods.

Phase I. SASS Train Evaluation

The SASS train evaluation test plan--starting with source selection criteria, continuing through sampling requirements, and ending with directions for sample analyses--is delineated in the following paragraphs.

Source Selection Criteria

Criteria used in the source selection process were:

1. The process stream should be sufficiently high in organics and particulate to provide a stiff challenge of the SASS train.

2. The process stream should be sufficiently stable to allow for comparison of data between days or runs.

3. The process stream must be amenable to this test in terms of: space for simultaneous operation of two SASS trains and a Method-5 train, available electrical power to operate the trains and two mobile laboratories, and a physical stack or duct configuration such that sampling port locations for Method 5 are consistent with criteria set forth in EPA Reference Method 1.[2]

Field Sampling

Samples were collected with the two SASS trains and the Method-5 train running simultaneously. Three complete sample runs were made. The relative positions of the trains were fixed with the probes of the two SASS trains positioned at a point of average duct velocity and within a few inches of each other. The Method-5 train was positioned downstream from the SASS trains and operated according to the Federal Register method, i.e., the duct was traversed and isokinetic sampling conditions were maintained.[3] The test site configuration is shown in Figure 1.

Analysis Scheme for Field Samples

To insure consistency, all analytical work for

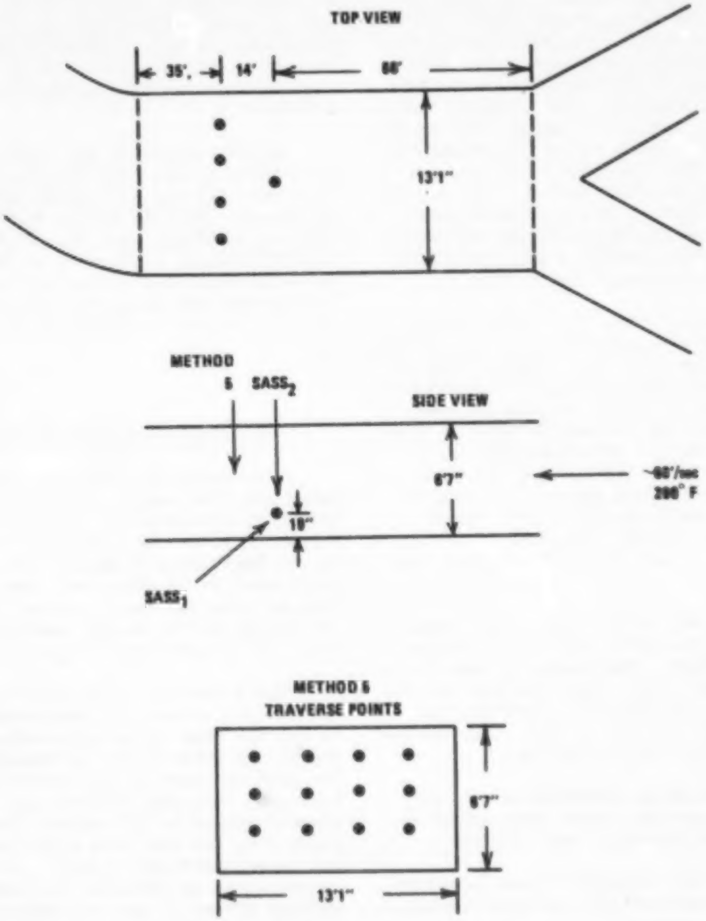


Figure 1. TEST SITE CONFIGURATION FOR FIELD EVALUATION OF THE SASS.

Phase I was done by one organization. Table 1 summarizes the analyses performed on one set of SASS runs. For the other two runs, the only analyses performed were gravimetric analyses of particulate for the cyclones, filter, and rinse. The analysis scheme of Table 1 is described in the following listing.

1. Particulate

    a. For each SASS train run, the particulate on the filter and in each cyclone was dryed, then weighed, and the total weight of particulate determined. The particulate for each Method-5 run was also dryed and weighed. Weighings were done in the field by one person. This allowed for a comparison of the SASS trains to each other and to the Method 5 for each run (same day) and on a day-today basis.

    b. For one test (two SASS trains and a Method-5 run simultaneously), the organics were extracted (soxhlet extraction) from the particulates and the particulates reweighed. The SASS particulate extracts were then analyzed for volatile (TCO) and nonvolatile (Grav) organic material, then subjected to a full Level-1 organics analysis, including LC-IR-LRMS.

2. XAD-2 Module

    a. For each SASS run, the total weight (TCO + Grav) was determined for the condensate and for the combined XAD-2 extract and module rinse.

    b. On the same pair of runs selected for the particulate organic analysis, the above TCO + Grav determinations were followed by eight class separations with a TCO + Grav determination on each of the fractions. The fractions were also analyzed by the IR-LRMS scheme.

3. Impingers

For the same pair of runs selected for particulate organics analysis and XAD-2 eight class separation, Hg, As, and Sb were determined on the combined second and third impingers by current Level-1 methods. No analyses were done on the impinger solutions for the remaining runs.

Phase II. Verification of the Analytical Scheme

Three sample types were supplied to each of the three participating organizations for analysis by current Level-1 procedures. The three sample types were:

1. A known artificial, liquid sample containing 8 to 10 components.

2. A real particulate sample obtained from a source significantly different from the one selected for Phase-I sampling.

Table 1. PROCEDURES FOR ANALYSIS OF A SELECTED PAIR OF SASS RUNS

SAMPLE	GC	DRY, WEIGH	SOXHLET EXTRACTION	DRY, RE-WEIGH	TCO + GRAV	LC	TCO + GRAV	IR-LRMS	PARR BOMB COMBUSTION	SSMS	As/Sb/Hg
10 µm CYCLONE		●									
3 µm CYCLONE		●	●	●	●	●	●	●			
1 µm CYCLONE		●									
FILTER		●									
XAD-2 CARTRIDGE			●								
ORGANIC RINSE (SORBENT MODULE)					●	●	●	●			
AQUEOUS CONDENSATE			●		●	●	●	●			
2ND AND 3RD IMPINGERS											●

3. The combined XAD-2 extracts from the SASS runs in Phase I.

Each participating organization was sent three aliquots each of the three above sample types for a total of nine samples per participant. The samples were coded and specific instructions for the analytical work to be done on each were provided. Each participant did a full Level-1 analysis on one aliquot of each of the above three sample types. For the other two aliquots of each type, there was a reduced analysis scheme.

Analysis Scheme for Control Samples

Procedures for analysis of the control samples for Phase II of the evaluation are summarized in Table 2 and discussed in the following paragraphs.

1. Sample 1

    a. Aliquot 1. This aliquot was taken through a complete Level-1 organic analysis beginning with a TCO + Grav. The sample was then separated into 8 fractions by LC with a TCO + Grav and IR-LRMS on each fraction.

    b. Aliquots 2 and 3. The analysis of these aliquots involved a TCO + Grav, 8 class separations by LC, and TCO + Grav on each of the 8 fractions.

2. Sample 2

    a. Aliquot 1. The analysis of this sample type followed the Level-1 scheme for particulates. One portion of the sample was extracted and a TCO + Grav performed on the extract. The extract was then separated into 8 fractions by LC and a TCO + Grav and IR-LRMS performed on each fraction. The remaining particulate was Parr-bomb combusted and analyzed by SSMS and by approved Level-1 procedures for AS/Hg/Sb.

    b. Aliquots 2 and 3. These two aliquots

were extracted and a TCO + Grav performed on the extract.

3. Sample 3

   a. Aliquot 1. Analysis of this combined extract sample started with a TCO + Grav followed by the 8 class LC separation and TCO + Grav IR-LRMS on each of the 8 fractions.

   b. Aliquots 2 and 3. These two aliquots involved only a TCO + Grav analysis.

Results of SASS Evaluation

The purpose of an interlaboratory test such as this is to, within the project constraints, determine:

1. Where possible, the comparability of the experimental system results with reference methods or standard material (accuracy),

2. Comparison of results between similar sets of equipment operated by different laboratories (reproducibility or interlaboratory precision), and

3. Comparison of duplicate results from the same system operated by the same laboratory (repeatability or intralaboratory precision).

At this time, all of the analytical data from the SASS evaluation are not available for this paper. Measurements for which data are available and the order in which they will be discussed are as follows:

1. Particulate concentration determinations allowing comparison of the SASS with Method 5 and comparison between SASS's for three runs.

2. Particle size fractionation between SASS's for three runs.

3. Organic material collected between SASS's for one run.

4. Total, volatile, and nonvolatile organics by LC fractions between SASS's for one run.

5. Organic categories in sample between SASS's for one run.

6. IR results (functional groups) for one sample between SASS's.

7. Number of subcategories and specific compounds identified by LRMS for one sample between SASS's.

Table 2. PROCEDURES FOR ANALYSIS OF PHASE II SAMPLES

	SOXHLET EXTRACTION	TCO + GRAV	LC	TCO + GRAV	IR-LRMS	PARR BOMB COMBUSTION	SSMS PLUS As/Hg/Sb
SAMPLE 1							
ALIQUOT 1		●	●	●	●		
ALIQUOTS 2 AND 3		●	●	●			
SAMPLE 2							
ALIQUOT 1	●	●	●	●	●	●	●
ALIQUOTS 2 AND 3	●	●					
SAMPLE 3							
ALIQUOT 1		●	●	●	●		
ALIQUOTS 2 AND 3		●					

8. Arsenic, mercury, and antimoney determinations for one sample between SASS's.

Particulate Concentration Determinations

Three complete sample runs were made with the two SASS's and the Method-5 train sampling simultaneously as described in the test plan discussion. Particulate concentration determined by each SASS and by Method 5 are given by run in Table 3.

Table 3. PARTICULATE CONCENTRATION mg/m^3

TRAIN / RUN #	SASS-1	SASS-2	M-5
RUN-1	408	337	342
RUN-2	399	349	322
RUN-3	353	315	371

σ = 28 mg/m^3 (8%) WITHIN TRAIN PRECISION.

$\sqrt{\sigma^2 + \sigma_t^2}$ = 36 mg/m^3 (10%) BETWEEN TRAIN PRECISION.

An analysis of variance (ANOVA) was performed to test at the 0.05 level of significance, the following hypotheses:

1. Hypothesis 1: there are no train effects.
2. Hypothesis 2: there are no run effects.

The ANOVA table is given in Table 4.

From the experimental data, the calculated F values are 1.48 and 0.13 for trains and runs, respectively. The tabulated value for $F_{0.95}$ (2,4) is 6.94. Therefore, neither of the previously stated hypotheses can be rejected. That is, based on this set of data we cannot say that the SASS's differ from each other or that either SASS differs from Method 5.

From the ANOVA, the best estimate of the precision of a single observation, regardless of train (intertrain precision), is $(\sigma^2 + \sigma_t^2)^{1/2}$ = 36 mg/m^3. The coefficient of variation (or relative standard deviation) is 0.10, or 10 percent.

Intratrain precision is estimated by σ and is equal to 28 mg/m^3.

The results of this evaluation show that for this one source the SASS's precision and accuracy were not significantly different from the precision and accuracy of the Method-5 determinations.

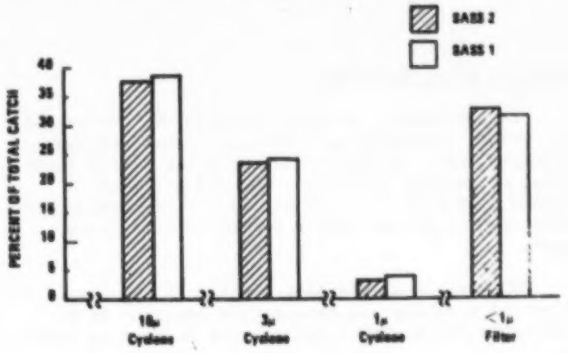
Table 4. ANALYSIS OF VARIANCE TABLE

Source	Sum of Squares	df	Mean Square	Estimate of
Runs	395	2	197	$\sigma^2 + 3\sigma_r^2$
Trains	4,674	2	2,337	$\sigma^2 + 3\sigma_t^2$
Residual	3,154	4	789	σ^2
Total	8,223	8		

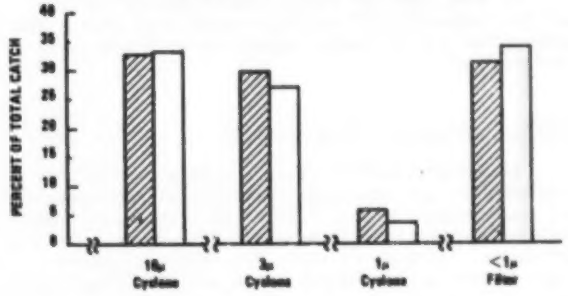
Particle Size Fractionation

Particulate matter is divided into four size fractions by the SASS using three cyclones and a filter in series. From Table 3 in the previous section, comparison of particulate concentrations measurements can be made. The particulate concentration, as determined from each cyclone and the filter, is given as a percent of the total concentration determined by the train in Figure 2.

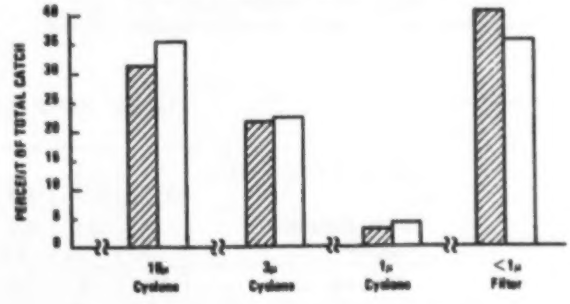
As seen from Figure 2, results from corresponding components of the SASS's compare very well for Runs 1 and 2. The significance of the differences, if they are significant, as shown by the 10μ cyclones and filters in Run 3 will have to be evaluated by individuals knowledgeable on particle size measurements.



COMPARISON OF PARTICLE SIZE FRACTIONATION (Run 1)



COMPARISON OF PARTICLE SIZE FRACTIONATION (Run 2)



COMPARISON OF PARTICLE SIZE FRACTIONATION (Run 3)

Figure 2. COMPARISON OF PARTICLE SIZE FRACTION OF TWO SASS's

Organic Extractables

Extracting organic matter from SASS samples is an important procedure in the analysis process. Table 5 compares the volatile (TCO) and nonvolatile (Grav) organic contents of the samples taken from corresponding components of the SASS's. The data show that organic material collected by the corresponding components was comparable in quantity (total) and in composition (volatile and nonvolatile).

Table 5. ORGANIC EXTRACTABLES (mg/m^3)

	CYCLONE		XAD-2 (EXTRACT)		XAD-2 (MODULE)	
	SASS-1	SASS-2	SASS-1	SASS-2	SASS-1	SASS-2
TCO	0.03	0.01	3.41	3.58	(RINSE)	
GRAV	1.65	1.58	10.2	8.96	69	81
TOTAL	1.7	1.6	13.6	12.6	69	81

Organics in LC Fractions

In the Level-1 analysis procedures, the sample extract is separated by silica gel liquid chromatography and a solvent gradient series into 8 fractions of varying polarity. TCO and gravimetric analyses of each fraction are done to determine the distribution of the sample by the various class types.

Comparison of the distribution of the sample in terms of volatile and nonvolatile organics by LC fractions for an XAD-2 extract can be seen in Table 6.

As seen from the table, the totals (Σ) across all fractions for TCO and Grav agree very well. The comparison for individual fractions with few exceptions is good.

Organic Categories Identification

Identifications of organic categories in process streams are important functions of environmental assessments. Table 7 lists the categories and their concentrations as determined from one set of SASS runs. As seen in the table, the categories compare well across trains, both qualitatively and quantitatively.

Qualitatively, only inorganics at 0.1 mg/m^3 and silicones at 0.1 mg/m^3 were identified in the SASS-1 sample and not the SASS-2 sample. Quantitatively, when the concentration levels are considered, only the difference in the heterocyclic O concentrations appears to be much larger than desired.

Functional Groups Identified by IR

IR spectnoscopy is used in the Level-1 environmental assessment procedures to determine the types of functional groups present in a sample. Table 8 shows the results of an IR analysis of the XAD-2 extract for SASS-2. A similar analysis for SASS-1 yielded almost identical results.

The wave number ν(cm^{-1}), the intensity level [weak (w), medium (m), or strong (s)], and functional group symbol or name are given in Table 8.

Subcategories and Compound Identification by LRMS

A low resolution mass spectrum (LRMS) is obtained on all LC fractions that exceed the concentration threshold in order to determine the principle compound types present in each fraction. A comparison of the number of compound types identified by both SASS's and by each SASS separately is given in Table 9 by LC fraction.

As seen in the totals of Table 9, out of a total of 41 compounds identified by one or both of the SASS's, 25 were identified by both SASS's. Thirteen compounds were identified in the SASS-1 sample only. Before a judgment is made on whether this is critical or not, the total SASS samples will have to be compared to determine if these 13 compounds were identified in samples from other parts of the SASS train. This point will be further studied and documented in the report to be issued at a later date.

Arsenic, Mercury, and Antimony Comparisons

Antimony and mercury are determined by atomic absorption, and arsenic is determined by the silver diethyldithiocarbonate (SDDC) method in the Level-1 procedures. Table 10 compares the levels of these elements found in the samples from the two SASS's. The estimates of precision of analysis were provided by Arthur D. Little, Inc. The agreement appears reasonable, based on the precision estimates for As and Sb. However, the difference in the Hg concentrations is larger than would be expected from analysis imprecision alone. The difference is less than a factor of two.

Table 6. XAD-2 EXTRACT SUMMARY

	(SASS-1/SASS-2)								
	LC1	LC2	LC3	LC4	LC5	LC6	LC7	LC8	Σ
TOTAL ORGANICS, mg/m^3	.54 .33	.71 2.4	8.1 8.8	.95 .59	.35 .25	1.5 .93	.47 .24	.01 .07	12.6 13.6
TCO, mg	5.2 2.6	19 35	73 58	6.7 1.7	3.7 1.1	5.3 5.7	0.1 0.1	0.2 2.1	113 106
GRAV, mg	13 7.5	3.3 38	182 216	23 17	7.3 6.7	41 23	15 7.3	0 0	284 315

Table 7. COMPARISON OF CATEGORIES FROM ORGANIC EXTRACTS

CATEGORIES	CONCENTRATION (mg/m³) SASS-1	 SASS-2
ALIPHATIC HYDROCARBONS	1.1	1.1
HALOGENATED AROMATIC HC'S		
AROMATIC HC'S - BENZENE	0.6	0.1
< 216	28.7	28.2
> 216	25.6	28.7
HETEROCYCLIC N	20.1	24.0
HETEROCYCLIC S	2.4	2.5
HETEROCYCLIC O	2.2	6.7
PHENOLS	0.2	0.3
ESTERS	0.5	0.2
ETHERS		
AMINES		
AMIDES		
CARBOXYLIC ACIDS	0.6	0.7
SULFONIC ACIDS, SULFOXIDES		
SULFUR	0.2	0.7
INORGANICS	0.1	
UNCLASSIFIED	0.3	1
SILICONES	0.1	

Table 8. FUNCTIONAL GROUPS IN SASS SAMPLE IDENTIFIED BY IR

υ, cm^{-1}	INTENSITY, ASSIGNMENT	
3400	Vw (br)	NH, OH
3050	M	AROMATIC, C-H
2950-30	M	ALIPHATIC, C-H
1700	W	ESTER, IMIDE, KETONE UNSUBSTITUTED AMIDINE HCl, CARBONATE
1600	M	C-N=0, N-C=N; RING VIBRATIONS
1500	W	RING VIBRATIONS
1460-1420	M	Si-AROMATIC, SCH_2^-, 3-SUBSTITUTED PYRIDINE, ALIPHATIC AND AROMATIC C-H, $SiCH_2^-$
1180	M	ESTER, SiO-CH_3, $C_3P=0$
850-700	S(MULTIPLE)	SUBSTITUTED AROMATIC OR FUSED RINGS

Table 9. SUBCATEGORIES AND SPECIFIC COMPOUNDS IDENTIFIED BY LRMS (XAD-2 EXTRACT)

FRACTION	SASS-1 AND SASS-2	SASS-1 ONLY	SASS-2 ONLY	TOTAL
LC1		3		3
LC2	10	3	1	14
LC3	11	6	4	21
LC4	13	5	2	20
LC5				
LC6	5	1	2	8
LC7		9		9
LC8				
LC1-LC8	25	13	3	75 41

Table 10. ARSENIC, MERCURY, AND ANTIMONY DETERMINATIONS

	As (µg/m³)	Hg (µg/m³)	Sb (µg/m³)
SASS-1	0.71	0.24	0.06
SASS-2	0.83	0.40	0.10

ESTIMATED PRECISION OF ANALYSIS
CV(As) = 5%, CV(Hg) = 10%, CV(Sb) = 25%

Results of Analytical Methods Evaluation

Evaluation of Level-1 environmental assessment methodologies for analysis of SASS samples was performed by providing control samples of three types to the participating laboratories. The control samples were prepared and analyzed by Arthur D. Little, Inc. Arthur D. Little's results are used as a fourth set of data for interlaboratory comparisons. Laboratories or participants are coded as A, B, C, and D, and are not further identified in this paper.

Data from all participants have not been available long enough to allow for a rigerous analysis of the results. Also, we are still in the process of developing means for presenting these large quantities of data in a meaningful and effective manner. Therefore, to provide an overview of the results of Phase II, and at the same time to hold this paper to a presentable length, only the data from the organic analysis of the real sample (sample 3, Table 2) and the SSMS results on aliquot 1 of sample 2 are presented here.

Organic Analysis Results

The order of discussion for organic analyses follows the analytical scheme presented in Table 2. That order is:

1. TCO + Grav analyses of the composite sample
2. TCO + Grav analyses of the LC fractions
3. IR analyses of LC fractions

4. LRMS analyses of LC fractions

TCO + Grav Analyses of Composite Sample

The first step in analyzing the XAD-2 extract is the determination of the volatile (TCO) and nonvolatile (Grav) organic contents in the sample. Table 11 compares the TCO and Grav values determined by the four participants for three aliquots or replications.

Table 11. ORGANIC CONTENTS IN XAD-2 EXTRACT, INITIAL VALUES

PARTICIPANT	TCO	GRAV	TOTAL
A	106 mg	386 mg	492 mg
B	78	380	458
C	88	359	447
D	150	340	490
A	144	343	487
B	64	432	496
C	110	366	476
D	86	360	446
A	142	354	496
B	46	428	474
C	118	380	498
D	134	360	494

Total organic (TCO + Grav) determinations show good agreement. The average and coefficient of variation (CV) for the 16 determinations are 480 mg and 4 percent, respectively. The range for the 16 values is only 52 mg or 11 percent of the average.

Determinations of nonvolatile organics showed good interlaboratory agreement. The average and CV for the 16 values is 374 mg and 8 percent, respectively.

TCO determinations show within laboratory CV's of 16, 26, 15, and 27 percent for participants A, B, C, and D, respectively. The agreement between participants A, C, and D are good. Participant B reports an average value of 63 mg, almost half of what the other participants reported.

TCO and Grav Analyses of the LC Fractions

Results of TCO and Grav analyses of the LC fractions (XAD-2 extract sample) are given in Table 12. The data indicate an overlap or "smearing" of fractions, resulting in differences in distribution among the four contractors. For example, the totals (TCO + Grav) for fraction 2 and for fraction 3 show large differences among the four contractors, whereas the sums of fractions 2 and 3 are fairly consistent.

Also worthy of note are the unexpected differences in %TCO across the four laboratories, ranging from 8 percent for laboratory B to 30 percent for laboratory C.

Identification of Functional Groups by IR

Two sets of IR data are presented here. One set is presented in Table 13 and represents a listing of the functional groups identified by three participants in the XAD-2 extract prior to LC separation. The other set of data is a graphical presentation of IR results by LC fraction and participant. The latter set of data is given in Figures 3 and 4.

From Table 13 it is seen that there is not a one-to-one agreement between participants. However, we feel that the comparisons are generally acceptable.

Examination of the data presented in Figures 3 and 4 reveals the same types of fractional overlaps as were noted in the TCO and Grav analyses. In addition, laboratories C and D report a number of bands that are not reported by laboratory A or B. A possible explanation is sample contamination or artifacts from the column, since laboratories C and D report recoveries greater than 100 percent for the TCO and Grav analyses of the LC fractions.

Categories Identification by LRMS

Categories identified in the XAD-2 extract by LRMS are shown in Table 14 by LC fractions for two participants. (Participants C and D did not run LRMS's on several LC fractions.) The LC fraction, the category name, and the relative intensity are given in the table. Intensities in decreasing order of intensity are recorded as 100, 10, or 1.

Table 12. TCO AND GRAV ANALYSES RESULTS BY LC FRACTION (mg)

	TCO				GRAV				TOTAL			
	A	B	C	D	A	B	C	D	A	B	C	D
LC-1	1.4	<0.4	12.0	2.1	11.5	4.0	4.8	–	13	4	17	2.1
LC-2	15.2	<0.4	60.3	120	4.6	6.4	84.6	200	20	6	145	320
LC-3	54.7	31	40.3	2.6	259	284	177.6	19	314	315	218	22
LC-4	0.5	2.3	9.2	1.4	10.1	22	12.8	–	11	24	22	1.4
LC-5	0.9	0.84	0.4	7.4	31.3	8.8	7.6	–	32	10	8	7.4
LC-6	3.2	1.0	18.4	13	16.6	38	27.1	110	20	39	46	123
LC-7	0.5	<0.4	21.6	1.9	2.8	23	23.1	–	3	23	45	1.9
LC-8	0.9	<0.4	N.R.	8.3	3.7	37	45.1	50	5	37	45	58
TOTAL	77	37	162	157	340	423	383	379	418	458	546	536

Table 13. FUNCTIONAL GROUPS IDENTIFIED BY IR ANALYSES OF XAD-2 EXTRACT

A			B			D		
3400	W	OH, NH	3800-3300	W	OH AND NH/TRACE	3420	W	AMINE, POSSIBLY CARBOXYLIC ACID
3050	M	UNSATURATED C-H	3100-3000	S	AROMATIC C-H	3050	S	AROMATIC C-H
2950, 2930, 2850	M	SATURATED C-H	3000-2800	M	ALIPHATIC C-H	29160, 2920, 2850	M	ALIPHATIC C-H
1730	W	KETONE, αCl KETONE, ESTERS	2000-1650	W	COMBINATION BANDS, AROMATIC			
			1710	M	C=0, ACIDS	1710	W	KETONES, ALDEHYDES, ESTERS
1600	M	RING VIBRATIONS, N-C=N				1600	M	ESTER, AMINE, AROMATIC OVERTONES
1500	W	RING VIBRATIONS	1585-1495	M	C=C, PHENYL RINGS			
1460-1430	M	CH_3, CH_2-Cl				1455 1440	M M	ALIPHATICS CARBOXYLIC ACIDS, ALIPHATICS
1380	W	CH_3						
1200	W(BROAD)	C-0, ESTER, ETHER, PHENOL				1240	W	ESTER, KETONE
						1180	W	ESTER, PHENOL
840,700	S(MULTIPLE)	SUBSTITUTED AROMATIC AND FUSED RINGS, PYRIDINE	900-700	S	γ(CH), AROMATIC RINGS	865,840	M	AMINE, AROMATIC SUBSTITUTION
740	S	C-Cl				815,780, 745,735	S	AROMATIC SUBS

Several of the categories correspond between participants as seen in the table. The most obvious difference is that participant B reported benzene in fractions 2 through 8 while participant A did not find benzene in any of the fractions. (Similarity of the IR spectrums of A and B for this sample indicates that this is an interpretation problem.)

Inorganic Analysis Results

The Phase-II flyash sample aliquots were Parr bombed in accordance with Level-1 procedures and sent to independent laboratories for analysis by spark source mass spectometry (SSMS). Results for selected elements are given in Table 15. In all but two of the cases shown (copper and chromium), the high and low values for a given element differ by a factor greater than 3. Nickel and beryllium, which have the lowest MATE values of the elements shown, were found to range from 13 to 380 ppm and from 0.5 to 14 ppm, respectively.

An intralaboratory comparison can be made using the data for contractors C and D since both SSMS analyses were performed by the same outside laboratory. Differences, however, could be partially attributed to sample preparation since the sample aliquots were Parr bombed by the individual contractors before being sent for SSMS analysis.

Included in the table are values for arsenic and antimony, two of the elements for which alternate procedures are specified in Level 1. A comparison of these SSMS values to the values obtained by the recommended silver diethyldithiocarbonate (SDDC) method for arsenic and the atomic absorption method for antimony is given in Table 16. For Sb, the values obtained by AA are slightly less than those by SSMS in both cases. For arsenic, however, the differences are much greater with the SDDC value being higher than the SSMS value in one case and lower in the other.

Summary

A brief summary of what we believe this preliminary analysis of the SASS evaluation indicates is as follows:

1. Particulate concentrations determined by the SASS's compared very well with Method 5 and with each other;

2. Particle sizing compared very well between SASS's;

3. Organic material collected by the SASS's agreed well in quantity and composition (i.e., volatile, nonvolatile, and categories), and was collected proportionally in corresponding SASS components.

The results of the analytical methods evaluation are interpreted as follows:

1. Certain methods employed in the organic

IR RESULTS: XAD-2 EXTRACT, FIELD SAMPLE

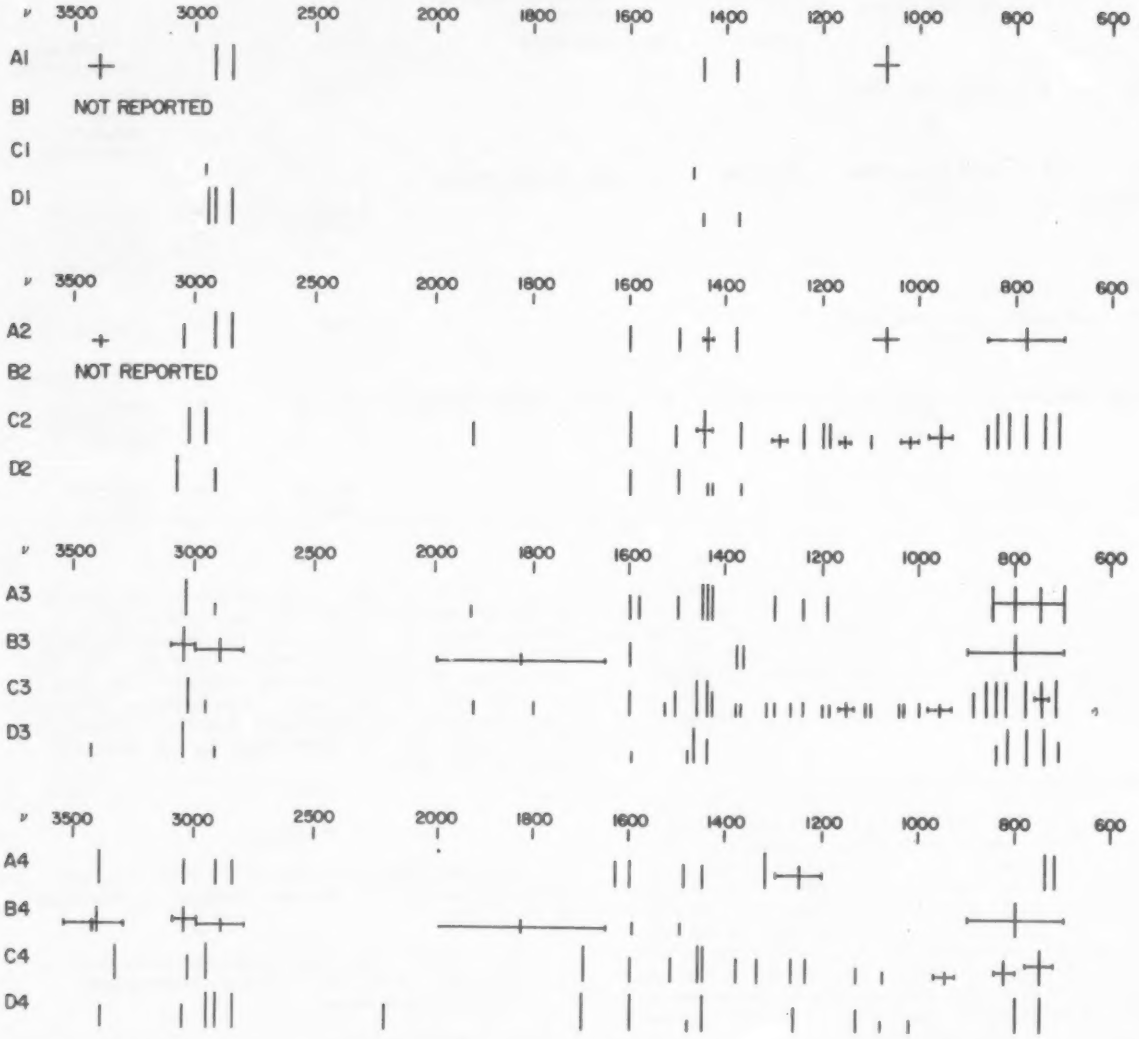


Figure 3. IR ANALYSES OF LC FRACTIONS 1-4

IR RESULTS: XAD-2 EXTRACT, FIELD SAMPLE

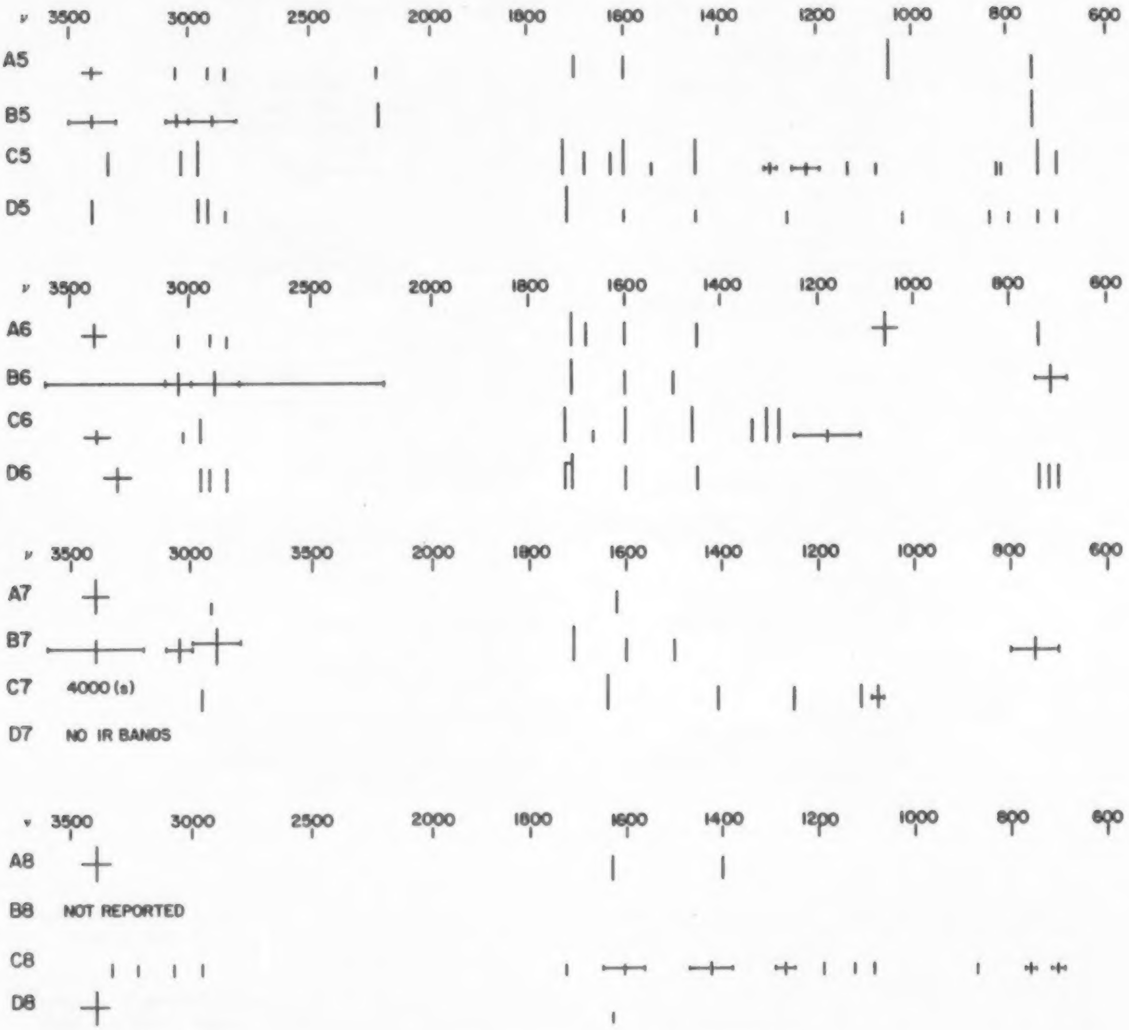


Figure 4. IR ANALYSES OF LC FRACTIONS 5-8

Table 14. CATEGORIES IDENTIFIED BY LRMS

	A	B
LC-1	• SULFUR (100) • ALIPHATIC HYDROCARBONS (1)	• SULFUR (100)
LC-2	• FUSED ALT/NON-ALT HYDROCARBONS, <m/e 216 (100) • FUSED ALT/NON-ALT HYDROCARBONS, >m/e 216 (10) • HETEROCYCLIC SULFUR COMPOUNDS (10)	• FUSED AROMATICS, MW<216 (100) • FUSED AROMATICS, MW>216 (10) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100) • HETEROCYCLIC NITROGEN COMPOUNDS (10)
LC-3	• FUSED ALT/NON-ALT HYDROCARBONS, <m/e 216 (100) • FUSED ALT/NON-ALT HYDROCARBONS, >m/e 216 (100) • HETEROCYCLIC SULFUR COMPOUNDS (10)	• FUSED AROMATICS, MW<216 (100) • FUSED AROMATICS, MW>216 (100) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100)
LC-4	• HETEROCYCLIC NITROGEN COMPOUNDS (100) • FUSED ALT/NON-ALT HYDROCARBONS, <m/e 216 (10) • FUSED ALT/NON-ALT HYDROCARBONS, >m/e 216 (10)	• FUSED AROMATICS, MW<216 (100) • FUSED AROMATICS, MW>216 (100) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100) • HETEROCYCLIC NITROGEN COMPOUNDS (10)
LC-5	• HETEROCYCLIC OXYGEN COMPOUNDS (100) • HETEROCYCLIC NITROGEN COMPOUNDS (100) • FUSED ALT/NON-ALT HYDROCARBONS, <m/e 216 (10)	• FUSED AROMATICS, MW<216 (100) • FUSED AROMATICS, MW>216 (100) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100) • NITRILES (100) • HETEROCYCLIC NITROGEN COMPOUNDS (100)
LC-6	• HETEROCYCLIC OXYGEN COMPOUNDS (100) • HETEROCYCLIC NITROGEN COMPOUNDS (100) • ESTERS (10) • CARBOXYLIC ACIDS (10) • PHENOLS (10)	• FUSED AROMATICS, MW<216 (100) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100) • NITRILES (100) • HETEROCYCLIC NITROGEN COMPOUNDS (100)
LC-7	• HETEROCYCLIC NITROGEN COMPOUNDS (100) • ESTERS (10) • CARBOXYLIC ACIDS (10) • HETEROCYCLIC OXYGEN COMPOUNDS (1)	• FUSED AROMATICS, MW<216 (100) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100) • NITRILES (100) • HETEROCYCLIC NITROGEN COMPOUNDS (100) • CARBOXYLIC ACIDS AND DERIVATIVES (100)
LC-8	• PHENOLS (10) • CARBOXYLIC ACIDS (1) • HETEROCYCLIC NITROGEN COMPOUNDS (1) • ETHERS (1) • ESTERS (1)	• FUSED AROMATICS, MW<216 (100) • FUSED AROMATICS, MW>216 (100) • BENZENE, SUBSTITUTED BENZENE HYDROCARBONS (100) • IRON (10)

analysis scheme are still being refined, and interpretation of the organic data from complex sources can be an involved process requiring great attention to detail. However, from this preliminary analysis of Phase-II data, it appears that the organic analysis scheme can yield results of adequate quality to satisfy Level-1 requirements, if judicious care is exercised by the analyst(s) to utilize all the analytical data generated by the scheme in interpreting individual blocks of data.

2. Results of the inorganic sample preparation and SSMS analysis scheme indicate that variability in the analytical phase alone may be exceeding the allowable factor of 2 or 3 in the Level-1 procedures.

Table 15. COMPARISON OF ANALYSIS OF SELECTED ELEMENTS BY SSMS (ppm, by weight)

ELEMENT	A	B	C	D
ARSENIC		41	38	140
ZINC		21	67	20
COPPER		42	41	120
NICKEL		69	380	13
COBALT		2.7	23	10
CHROMIUM		88	160	100
VANADIUM		58	28	130
CHLORINE		210	68	290
BERYLLIUM		0.8	0.5	14
URANIUM		2.5	3	90
THORIUM		5.1	8	75
LEAD		33	8	24
DYSPROSIUM		9.4	2	25
CERIUM		23	12	170
LANTHANUM		18	19	180
ANTIMONY		6.9	1	0.8

Table 16. COMPARISON OF As AND Sb BY SSMS AND BY SDDC AND AA, RESPECTIVELY*

	As (ppm)		Sb (ppm)	
	SDDC	SSMS	AA	SSMS
C	775	38	<1	1
D	35	140	<0.05	0.8

*SSMS determinations for contractors C and D were done by the same outside laboratory.

References

1. EPA-600/2-76-160a, "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, N.C. 27711, June 1976.
2. "Method 1--Sample and Velocity Traverses for Stationary Sources," Federal Register, Volume 42, No. 160, (Thursday, August 18, 1977), p. 41755.
3. "Method 5--Determination of Particulate Emissions From Stationary Sources," Federal Register, Volume 42, No. 160, (Thursday, August 18, 1977), p. 41776.

Acknowledgement

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INORGANIC EMISSIONS MEASUREMENTS

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Abstract. The analysis of inorganic compounds requires the coordinated use of a variety of analytical techniques. This paper describes an inorganic analysis scheme consisting of an initial sample characterization (stability, elemental composition, and morphology), bulk composition characterization (anion composition, surface characterization, and x-ray diffraction data) and individual particle characterization (single particle elemental composition, x-ray diffraction pattern, and morphology). The use of Multimedia Environmental Goal (MEG) compounds and their Minimum Acute Toxicity Effluent (MATE) values to focus analysis activities will be described. Data from a recent field test using this approach will be used to illustrate the information derived from these methods.

Introduction. With the increasing awareness of the government and scientific community to the possible hazards from the output of various industries, the Environmental Protection Agency has developed an approach to assess the environmental impact of any type of industrial process. This approach consists of a two phase attack. The first phase surveys the site to determine whether or not a given pollutant is being emitted. This so called Level 1 approach uses sampling and analysis methods to obtain results accurate to a factor of two to three. A set of criteria are used to prioratize the streams so that those streams which are found to be a problem are identified for further study. This next phase, Level 2, is designed to be specific for a given stream and perhaps for even a given pollutant. Compared to this phased approach, a direct environmental assessment of a site would use comprehensive sampling and analytical methods to determine all pollutants that are present with high accuracy. Figure 1 summarizes the difference between taking a phased approach or the direct approach environmental assessment. TRW has studied the two approaches and found significant cost savings by using the phased approach.[2]

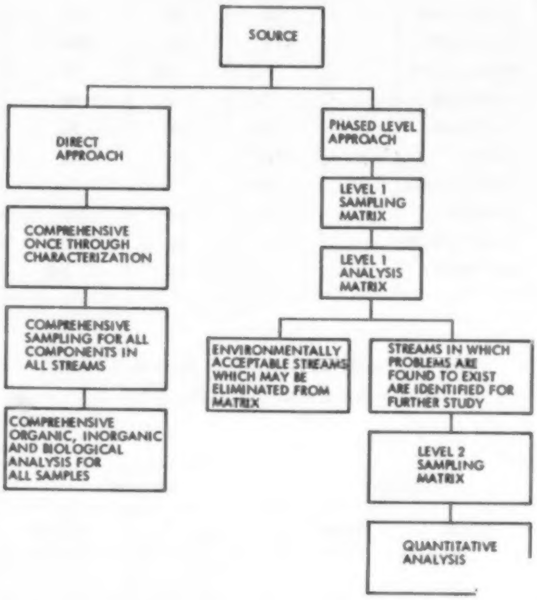
Level 1 Sampling and Analysis. The types of samples that will be obtained during a Level 1 sampling program can be broken down into four areas:

- Gaseous Samples — Process or fugitive emissions
- Liquid or Slurry Samples — Liquids or liquids with suspended solids
- Solid Samples — Solid holding or transfer systems
- Particulate Samples — Process or fugitive emissions

FIGURE 1

ENVIRONMENTAL ASSESSMENT

DIRECT VERSUS PHASED APPROACH

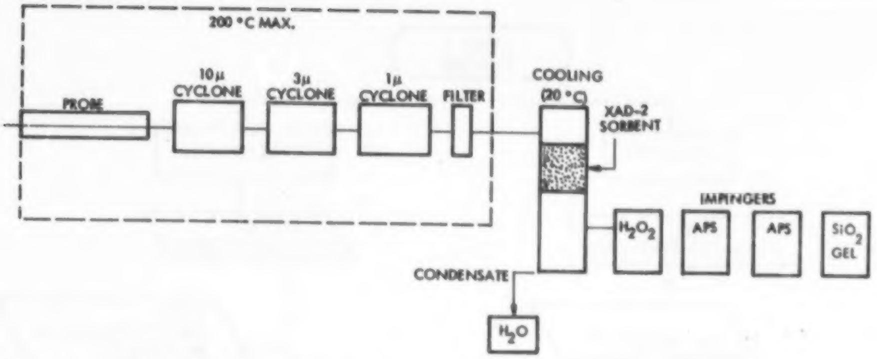

SOURCE
DIRECT APPROACH
COMPREHENSIVE ONCE THROUGH CHARACTERIZATION
COMPREHENSIVE SAMPLING FOR ALL COMPONENTS IN ALL STREAMS
COMPREHENSIVE ORGANIC, INORGANIC AND BIOLOGICAL ANALYSIS FOR ALL SAMPLES
PHASED LEVEL APPROACH
LEVEL 1 SAMPLING MATRIX
LEVEL 1 ANALYSIS MATRIX
ENVIRONMENTALLY ACCEPTABLE STREAMS WHICH MAY BE ELIMINATED FROM MATRIX
STREAMS IN WHICH PROBLEMS ARE FOUND TO EXIST ARE IDENTIFIED FOR FURTHER STUDY
LEVEL 2 SAMPLING MATRIX
QUANTITATIVE ANALYSIS

Gaseous samples are taken using a grab bag and analyzed on site for SO_2, H_2S, COS, CO, CO_2, O_2, NH_3, HCN and $(CN)_2$. A chemiluminescence detector is used for NO_x on-line measurement. Liquid or slurry streams are sampled using standard ASTM procedures. For particulate samples taken from flue gas streams, a specific train has been designed to collect the organic and inorganic components of the stream. The Source Assessment Sampling System (SASS), shown in Figure 2, is a comprehensive inorganic/organic sampling train consisting of a particulate and gaseous sampling sections. The particulate sampling section consists of a probe, 10, 3 and 1 μ micron cut-off cyclones. These cyclones are followed by a glass fiber filter which traps most particles down to a 0.3 μ with 99.9% efficiency. The entire particulate section is heated to 200°C to minimize H_2SO_4 condensation.

The gases from the particulate collection section are passed through a condensation module containing a cooling section and XAD-2 resin, which removes volatile organics above C_6. Inorganic materials which are removed from the gas phase by the condensing moisture are collected in the condensate trap. After the gases pass through the condensation module they encounter an oxidative impinger train. This oxidative impinger train is designed to trap all volatile inorganic materials such as Hg, Cd, or As which conceiveably could pass through the cooling module. The oxidative impinger systems consists of

FIGURE 2

SASS TRAIN SCHEMATIC


200 °C MAX.
PROBE
10μ CYCLONE
3μ CYCLONE
1μ CYCLONE
FILTER
COOLING (20 °C)
XAD-2 SORBENT
IMPINGERS
H_2O_2
APS
APS
SiO_2 GEL
CONDENSATE
H_2O

peroxide impinger followed by two ammonium persulfate, silver catalyzed impingers. This impinger system has been tested thoroughly and is essentially 100 percent efficient for volatile inorganic materials.

Once the samples have been obtained from the field, they are either analyzed on site or returned to the laboratory for further analysis. Figure 3 shows the overview of the inorganic and organic analyses performed on gases, liquids, or solids. Primarily, gaseous analysis of inorganic materials relies on an on-site, GC for the combustion gas analysis. Spark Source Mass Spectrometery (SSMS) is the key inorganic analytical technique. All the liquids and solids are analyzed by SSMA for their elemental content. The SSMS results are supplemented by wet chemical techniques for Hg, As, and Sb, for improved accuracy on these elements. Liquids obtained on site are analyzed for selected anions (NO$_3^-$, Cl, F$^-$, CN$^-$ and SO$_4^=$) using field test kits.

Transition to Level 2. Once all the Level 1 samples have been analyzed, some method of correlating and evaluating these data is necessary. Figure 4 shows the decision procedure for proceeding from Level 1 to Level 2. In this procedure, analysis of the

FIGURE 3

LEVEL 1 MULTIMEDIA ANALYSIS OVERVIEW

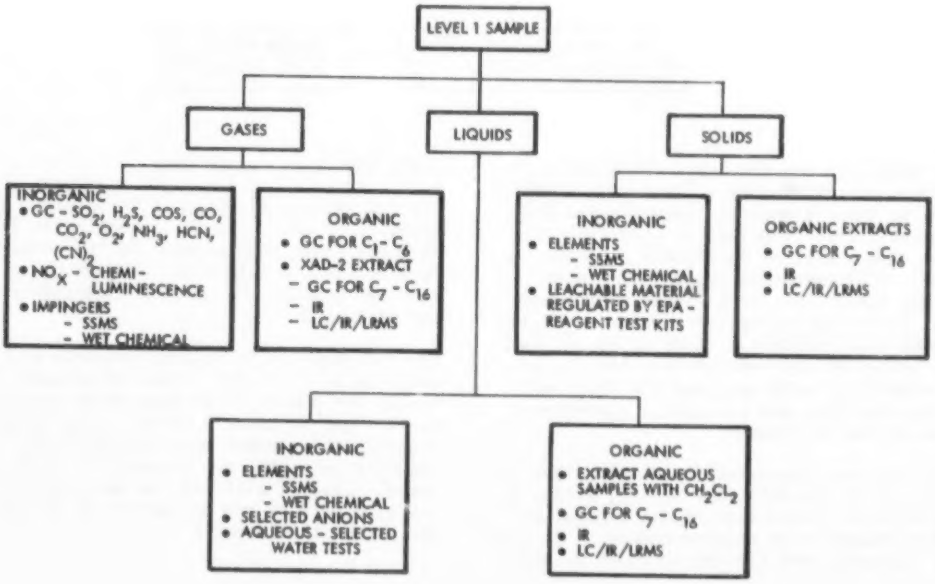
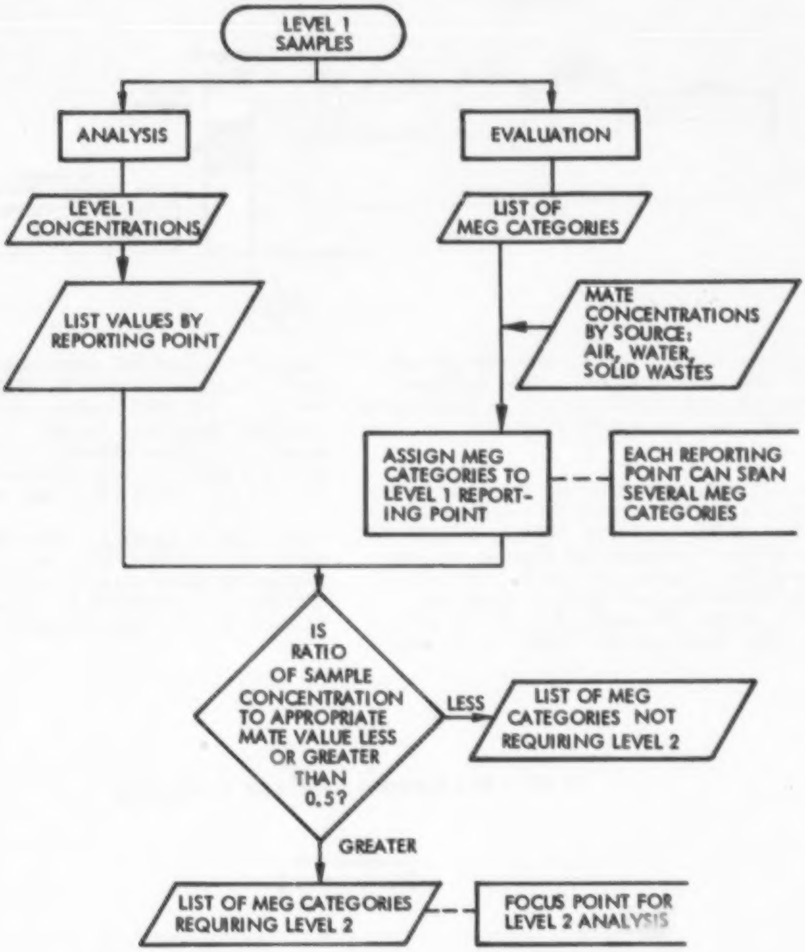

LEVEL 1 SAMPLE
GASES
LIQUIDS
SOLIDS
INORGANIC
• GC - SO_2, H_2S, COS, CO, CO_2, O_2, NH_3, HCN, $(CN)_2$
• NO_X - CHEMI-LUMINESCENCE
• IMPINGERS
- SSMS
- WET CHEMICAL
ORGANIC
• GC FOR C_1 - C_6
• XAD-2 EXTRACT
- GC FOR C_7 - C_{16}
- IR
- LC/IR/LRMS
INORGANIC
• ELEMENTS
- SSMS
- WET CHEMICAL
• LEACHABLE MATERIAL REGULATED BY EPA - REAGENT TEST KITS
ORGANIC EXTRACTS
• GC FOR C_7 - C_{16}
• IR
• LC/IR/LRMS
INORGANIC
• ELEMENTS
- SSMS
- WET CHEMICAL
• SELECTED ANIONS
• AQUEOUS - SELECTED WATER TESTS
ORGANIC
• EXTRACT AQUEOUS SAMPLES WITH CH_2Cl_2
• GC FOR C_7 - C_{16}
• IR
• LC/IR/LRMS

FIGURE 4

DECISION PROCEDURE FOR LEVEL 1 → LEVEL 2


LEVEL 1 SAMPLES
ANALYSIS
EVALUATION
LEVEL 1 CONCENTRATIONS
LIST OF MEG CATEGORIES
LIST VALUES BY REPORTING POINT
MATE CONCENTRATIONS BY SOURCE: AIR, WATER, SOLID WASTES
ASSIGN MEG CATEGORIES TO LEVEL 1 REPORTING POINT
EACH REPORTING POINT CAN SPAN SEVERAL MEG CATEGORIES
IS RATIO OF SAMPLE CONCENTRATION TO APPROPRIATE MATE VALUE LESS OR GREATER THAN 0.5?
LESS
LIST OF MEG CATEGORIES NOT REQUIRING LEVEL 2
GREATER
LIST OF MEG CATEGORIES REQUIRING LEVEL 2
FOCUS POINT FOR LEVEL 2 ANALYSIS

samples is completed and the Level 1 inorganic concentrations are determined. These values are then listed by their elemental concentration in $\mu g/m^3$ (gaseous), $\mu g/l$ (liquids) or $\mu g/g$ (solids). At the same time a list of Multimedia Environmental Goals (MEG) compounds are compiled with their Minimum Acute Toxicity Effluent (MATE) concentrations listed by source,(air, water or solid).[3] MEG compounds resulted from a study of fossil fuel conversion processes and represents a listing of compounds associated with coal and oil that could, based on free energies and conversion conditions, be released to the environment.

MATE's describe very approximate concentrations for contaminants in source emissions to air, water, or land which will not evoke significant harmful or irreversible responses in exposed humans or ecology, when those exposures are limited to short duration (less than 8 hours per day).

The sample concentration is the divided by the appropriate MATE value. If this ratio is greater than 0.5, then that element in the stream deserves further Level 2 attention. The value of 0.5 was selected because the Level 1 uncertainty is a factor of 2 to 3.

Level 2 analysis is focused research because we are able to limit the number of elements and potentially the number of streams which need to be re-examined in Level 2 tests. Level 2 will seek to quantify the element more exactly (±25%) and secondly determine the compound in which it is found. Level 2 will require more sophisticated analysis methods and an analyst to assess the data and direct the research.

Level 2 Sampling. In some cases it might be possible to analyze Level 1 samples further using Level 2 type techniques. In many cases because the SASS train is an all stainless steel train, these samples will be contaminated with Ni, Cr and Fe. Consequently a Level 2 inorganic particulate train can be used to sample streams which have been targeted for further research. This train, shown in Figure 5, is an all glass construction train. This train has been used in field tests and because of its all glass design Ni, Cr and Fe can be monitored. The train itself consists of a particulate section which has a 3μ cutoff cyclone, and a glass fiber filter. The particulate section is then backed up by a series of oxidative impingers which use the same chemistry as the SASS train. The main drawback with these glass trains is that they currently are designed to sample at 1 cfm. This low sampling rate compared to the SASS train is partially offset by the high sensitivity of most inorganic sampling techniques for elemental analysis.

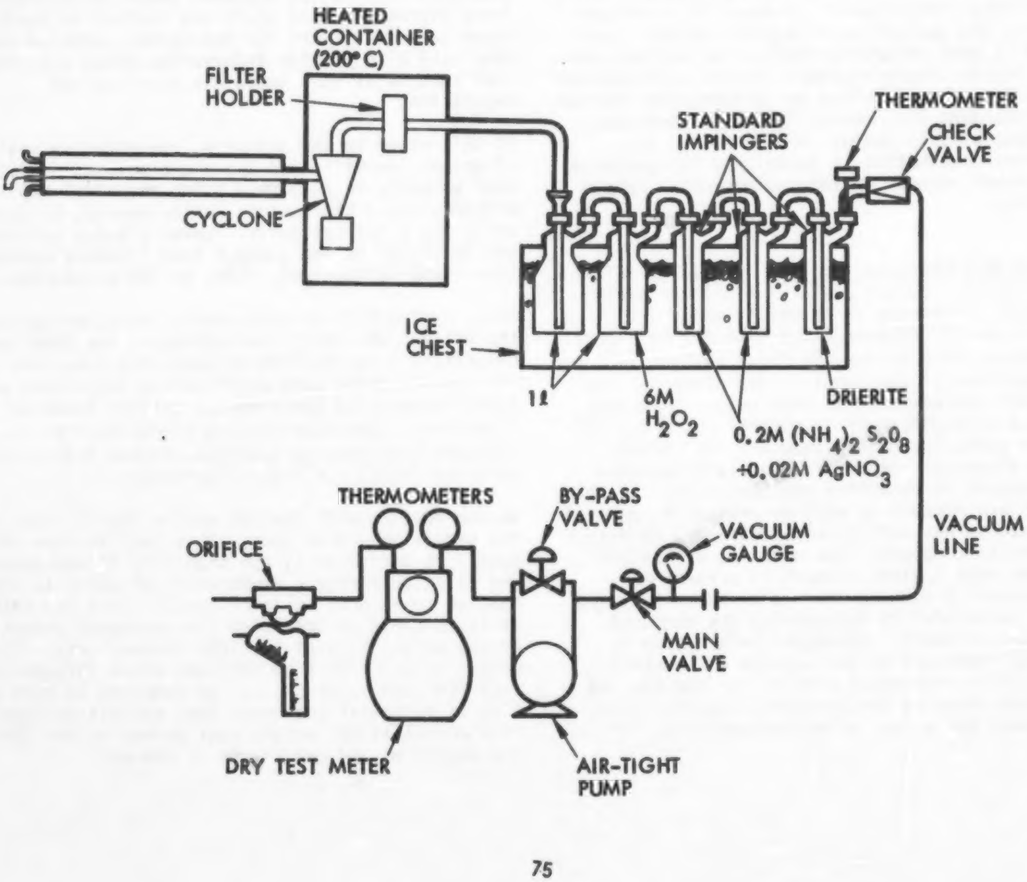
For other streams the improvement in sampling is not so much in the sampling system as it is in the design of the sampling program. Level 2 seeks to improve the representativeness of the sample taken by taking composited samples or timing the sampling to a specific phase of the process. The option is always available to design out of the ordinary equipment and procedures to obtain specific samples or to meet difficult sampling conditions. Level 2 should be free to meet the needs of specific situations and, like the Level 2 analysis, will require expert personnel to design the equipment and procedures.

Level 2 Analysis. The analysis of inorganic compounds requires the coordinated use of a variety of analytical techniques. Some techniques, such as XRD, TEM-SAED and ESCA, have the potential for direct compound identification, but only for selected compounds. The methods are of increasing analytical complexity, designed to be cost and time effective. The identification scheme consists of:

- Initial Sample Characterization — elemental composition, sample stability, and bulk morphological structure are determined.
- Bulk Composition Characterizations — qualitative and quantitative anion, oxidation state, and X-ray diffraction information are derived.
- Individual Particle Characterization — single particle elemental composition, X-ray diffraction pattern and morphology are measured.

FIGURE 5

LEVEL 2 INORGANIC SAMPLING TRAIN (GLASS)



The degree to which each method can be applied varies considerably with the experience, sample quantity and equipment available to the analyst. It is recommended that continuing use of any one method be evaluated in light of the information derived. In general, it is far better to use a variety of instruments operated in the most efficient manner rather than pushing a single instrument or technique to the limit of its capabilities.

In the Level 2 approach, emphasis is placed on reaching an accurate closure to the MEG compounds which exceed MATE values after a method or series of methods has been applied, a comparison of lists of identified to potential MEG compounds for elements which exceed their MATE values is made. A satisfactory analysis will depend upon a variety of factors:

- Number of MEG compounds identified exceeding MATE values
- Interest in identifying the remaining compounds for those elements that have exceeded MATE values
- Cost/availability of necessary equipment

The analyst must decide as to what method will be applied and how much more information can be obtained by each further analysis. In many cases some methods can be bypassed because of results from previous tests, e.g., quantitative anion analysis may provide sufficient information and FTIR would be only repetitious. In other cases efforts may direct the analyst to a specific method since it would be best suited to analyze for a given compound. The following sections provide a discussion of the proposed methodology and information derived. By understanding the outputs from each technique, the analyst will be better able to select the appropriate combination of techniques to determine the compounds present in the environmental sample of interest.

Initial Sample Characterization. Initially information from all sources (Level 1 field and analytical data) concerning the composition of the sample is pooled, assessed, and used for reference. This information provides the first insight into the composition of the sample. The elemental concentrations are compared to MATE values to determine which compounds must be sought. Once the MEG compounds exceeding MATE values are identified, then the elemental composition data will be used by the analyst to determine whether or not specific compounds are present as well as indicating whether a given method has sufficient sensitivity to detect the potential compound. For example, if the SSMS data shows that a given element is present at levels above 0.5 percent then bulk analysis by XRD might be successful in determining the compound form of this element. Elemental information is especially important to XRD because diffraction patterns of environmental samples are complex and information reducing the potential possibilities is necessary for a cost effective analysis.

Besides the SSMS data, there are several other sources of information that should be assembled. This information includes:

- Source of the sample: process type, e.g., oxidizing or reducing conditions.
- Composition of feed source: input raw materials e.g., coal, limestone.
- Previous history of sample: age, storage conditions, collection method.
- Results of previous analyses at this source: elemental and compound information.

As soon as the sample is in the laboratory, it should be viewed under a polarized light microscope (PLM) and a photomicrograph taken in color to act as quality control. If any changes in the general appearance of the sample occur, during the duration of the analytical activities, these should be noted. The PLM can also provide a measure of the complexity of the sample simply by noting the number of different types of particles.

Polarized light microscopy is the first direct compound analysis method. Particles can be identified by the determination of such properties as the refractive index, isotropy or anisotropy, birefringence, pleochroism, fracture, color, and crystal habit. Microspot tests for common anions and tests of the solubility of the particles in water, acid, and base can be performed directly on the sample as it is being examined under the microscope. These microtests will alert the analyst to perform quantitative analyses for the anions detected and they will also provide information about the potential success of full scale dissolutions and separation.

At this stage in the analysis, quantitative analysis of anions identified in the microspot tests will most probably be performed using classical wet test methods, e.g., titrimetric, colorimetric, or specific ion electrode tests. Level 2 anion methods can be chosen by the analyst from Standard Methods (Water and Wastewater), ASTM, or EPA procedures.

Also, during this initial sample characterization, the analyst may choose to supplement the SSMS semi-quantitative cation data by analyzing fractions of the samples using such quantitative techniques as atomic absorption spectrometry (either flame or flameless), Induction Coupled Plasma Optical – Emission Spectroscopy (ICPOES), Proton Induced X-Ray Emission (PIXE), or X-ray fluorometry.

In conjunction with the PLM work a TGA/DSC scan of the sample should be made. This test is used primarily to determine 1) the stability of the sample, and 2) an appropriate temperature at which to dry samples to be used in later tests. In a few cases it is possible to determine the compounds present by the weight loss at specific temperatures. Elemental information from SSMS and anion information from PLM (and later IR) can be combined to give a list of potential compounds that exhibit decomposition points at the weight loss points in the TGA or the exotherms and endotherms of the DSC.

At the end of the initial effort, information will have been obtained in the following areas:

1. General appearance of a sample
2. Number of different particles present
3. Index of refraction and crystal structure
4. Individual particle anion composition
5. Individual particle solubilities
6. Weight loss with respect to temperature
7. Bulk elemental distribution.

This exercise in logic is summarized in Figure 6.

Bulk Composition Characterization. Supposing that the need of the analyst to identify a specific pollutant has not been met, then the next phase of analysis, bulk characterization is started. The methods used in this approach are:

- X-Ray Diffraction (XRD)
- Fourier Transform IR (FTIR)
- Electron Spectroscopy for Chemical Analysis (ESCA).

To guide the analyst, a logic network for their application is shown in Figure 7.

It is expected that the samples will have to be dried to a constant water content to improve both IR and XRD spectra. Information from the TGA/DSC step will be used to select a drying temperature that removes water without decomposing the sample. Further sample preparation will vary with the requirements of the specific analysis method.

For IR analysis, the KBr pellet technique for qualitative analysis is not recommended due to ion exchange possible during the pelleting process. It is recommended that a Nujol null of the sample and AgCl (1333-400 cm^{-1}) and polyethylene (600-45 cm^{-1}) windows be used. Interpretation of the infrared spectra on the basis of characteristic frequencies can provide the identity of specifications and some of the individual compounds.

Extensive compilations of inorganic compounds are available (Ref #4). There are definite analytical frequencies which can be used to identify compounds, particularly when supporting elemental analysis information is available.

Electron spectroscopy for chemical analysis (ESCA) can be performed on both loose particulates and particles collected on filters. Loose particulate samples can be attached to a sample holder using an approach called the "sticky gold" technique. This technique was devised to overcome the conductivity problem and securely mount the sample. It sandwiches the sample between a layer of sputtered gold and carbon. The gold first layer applied to a double sided scotch tape does not change the tackiness of tape, which allows loose particles to be stuck to the surface. A layer of carbon is deposited on the surface assuring that all the particles are near a conductive surface. Filter pieces can be clamped directly onto the sample holder after the bottom layers of the filter have been peeled off.

In a recent sampling Level 2 sampling program taken at a coal-fired boiler with a flue gas desulfurization unit, and ESCA analysis was performed on a filter sample taken from the outlet of the FGD. During the analysis of this sample it was etched with Ar ions and the sulfur content, after each layer of the particle was removed, was analyzed using ESCA. Figure 8 shows the depth profile of the sulfur content. The intensity is a ratio of the sulfur 2s electron to the aluminum 2s electron. As one can see in the figure there is a definite depth profile with increasing sulfur content on the surface of the particle. In another case with some samples from a Fluidized Bed Combustor (FBC), a layer of sulfate was found to cover a sulfide particle. This information illustrates the capability of ESCA to determine the oxidation state of elements. By knowing the oxidation state of the element, the species that the element exists as can be determined.

The performance of specific anion tests, IR analysis, and ESCA establishes substantial information on the variety and depth profile of anions in the sample. This information simplifies interpretation of the XRD spectra, and provides an independent quantification of the species present. In X-Ray diffraction analysis, approximately 100 mg of material are ground in an agate mortar, ultrasonically dispersed with a 1:4 mixture of collodion with alcohol and then evenly spread over a glass support. Mounting in this fashion will produce the highest sensitivity at low 2θ values. The major disadvantage of XRD as an analytical tool is its inability to detect noncrystalline materials. In many environmental samples, the crystal structure of a compound could be grossly affected by the conditions at the source or those during sampling. For example, As_2O_3 can be amorphous or crystalline depending on its temperature history. Furthermore, the sensitivity of XRD is normally limited to 1 percent or higher, although new computer averaging techniques enable materials to be detected in concentrations as low as 0.05 percent. (5)

Having completed these analyses, information will have been obtained on the following:

1. Anions present
2. Valence state of elements present
3. Elemental depth profile
4. Major compounds present.

At this point the analyst must correlate all data and determine if a reasonable (based on the analyst's judgement) agreement has been reached with MEG elements exceeding their MATE values. If there is reasonable agreement between the elemental data obtained from quantitative techniques and the compounds determined in this characterization, further work should be carefully evaluated in terms of potential needs and end use.

FIGURE 6

LOGIC FLOW CHART FOR INITIAL SAMPLE CHARACTERIZATION

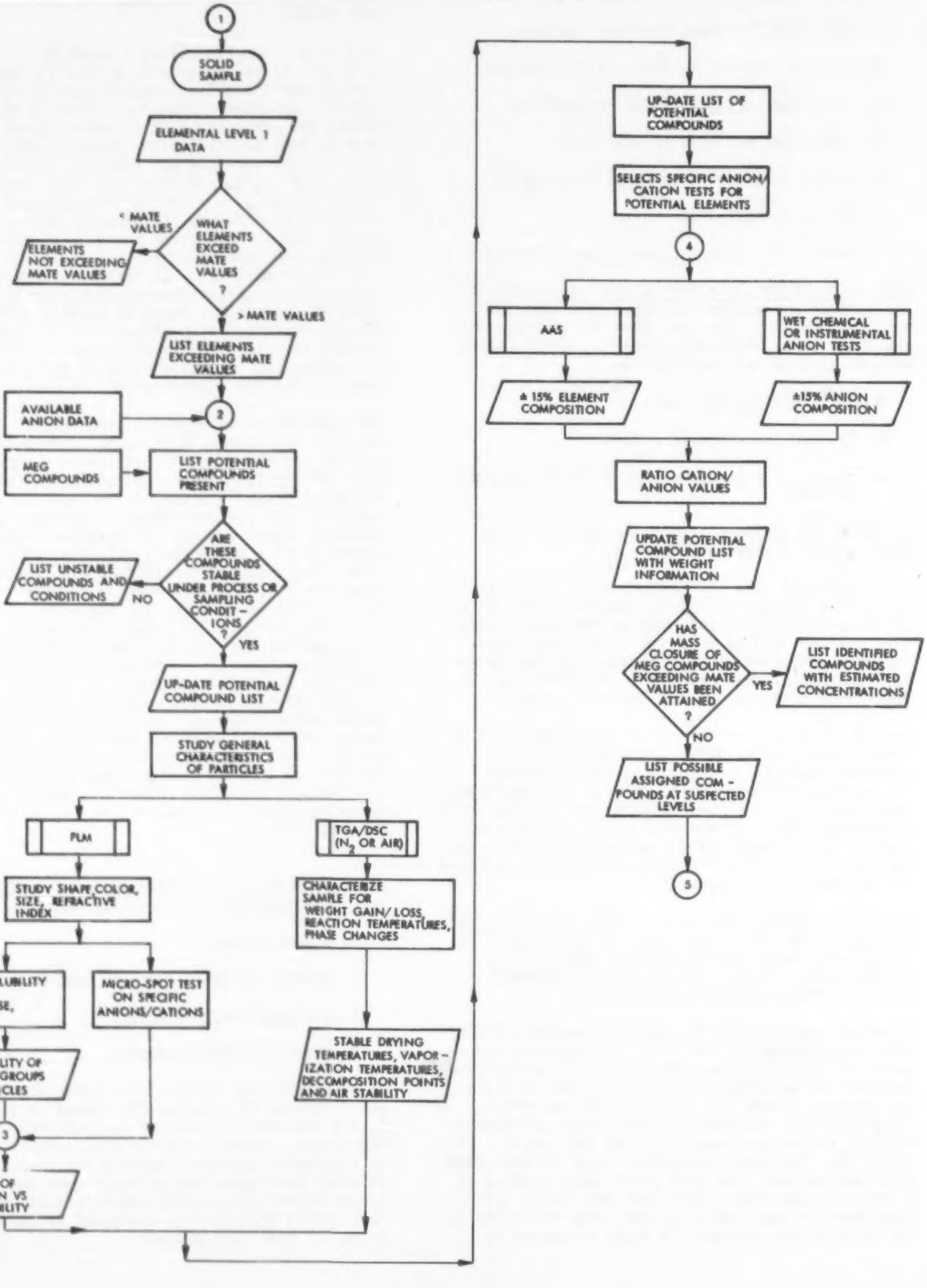

1
SOLID SAMPLE
ELEMENTAL LEVEL 1 DATA
WHAT ELEMENTS EXCEED MATE VALUES ?
< MATE VALUES
ELEMENTS NOT EXCEEDING MATE VALUES
> MATE VALUES
LIST ELEMENTS EXCEEDING MATE VALUES
AVAILABLE ANION DATA
2
MEG COMPOUNDS
LIST POTENTIAL COMPOUNDS PRESENT
ARE THESE COMPOUNDS STABLE UNDER PROCESS OR SAMPLING CONDIT - IONS ?
NO
LIST UNSTABLE COMPOUNDS AND CONDITIONS
YES
UP-DATE POTENTIAL COMPOUND LIST
STUDY GENERAL CHARACTERISTICS OF PARTICLES
PLM
TGA/DSC (N_2 OR AIR)
STUDY SHAPE, COLOR, SIZE, REFRACTIVE INDEX
CHARACTERIZE SAMPLE FOR WEIGHT GAIN/ LOSS, REACTION TEMPERATURES, PHASE CHANGES
MICROSOLUBILITY TESTS (ACID, BASE, NEUTRAL
MICRO-SPOT TEST ON SPECIFIC ANIONS/CATIONS
SOLUBILITY OF SPECIFIC GROUPS OF PARTICLES
3
LISTS OF ANION VS SOLUBILITY
STABLE DRYING TEMPERATURES, VAPOR - IZATION TEMPERATURES, DECOMPOSITION POINTS AND AIR STABILITY
UP-DATE LIST OF POTENTIAL COMPOUNDS
SELECTS SPECIFIC ANION/ CATION TESTS FOR POTENTIAL ELEMENTS
4
AAS
WET CHEMICAL OR INSTRUMENTAL ANION TESTS
± 15% ELEMENT COMPOSITION
±15% ANION COMPOSITION
RATIO CATION/ ANION VALUES
UPDATE POTENTIAL COMPOUND LIST WITH WEIGHT INFORMATION
HAS MASS CLOSURE OF MEG COMPOUNDS EXCEEDING MATE VALUES BEEN ATTAINED ?
YES
LIST IDENTIFIED COMPOUNDS WITH ESTIMATED CONCENTRATIONS
NO
LIST POSSIBLE ASSIGNED COM - POUNDS AT SUSPECTED LEVELS
5

FIGURE 7

LOGIC FLOWCHART FOR BULK COMPOSITION CHARACTERIZATION

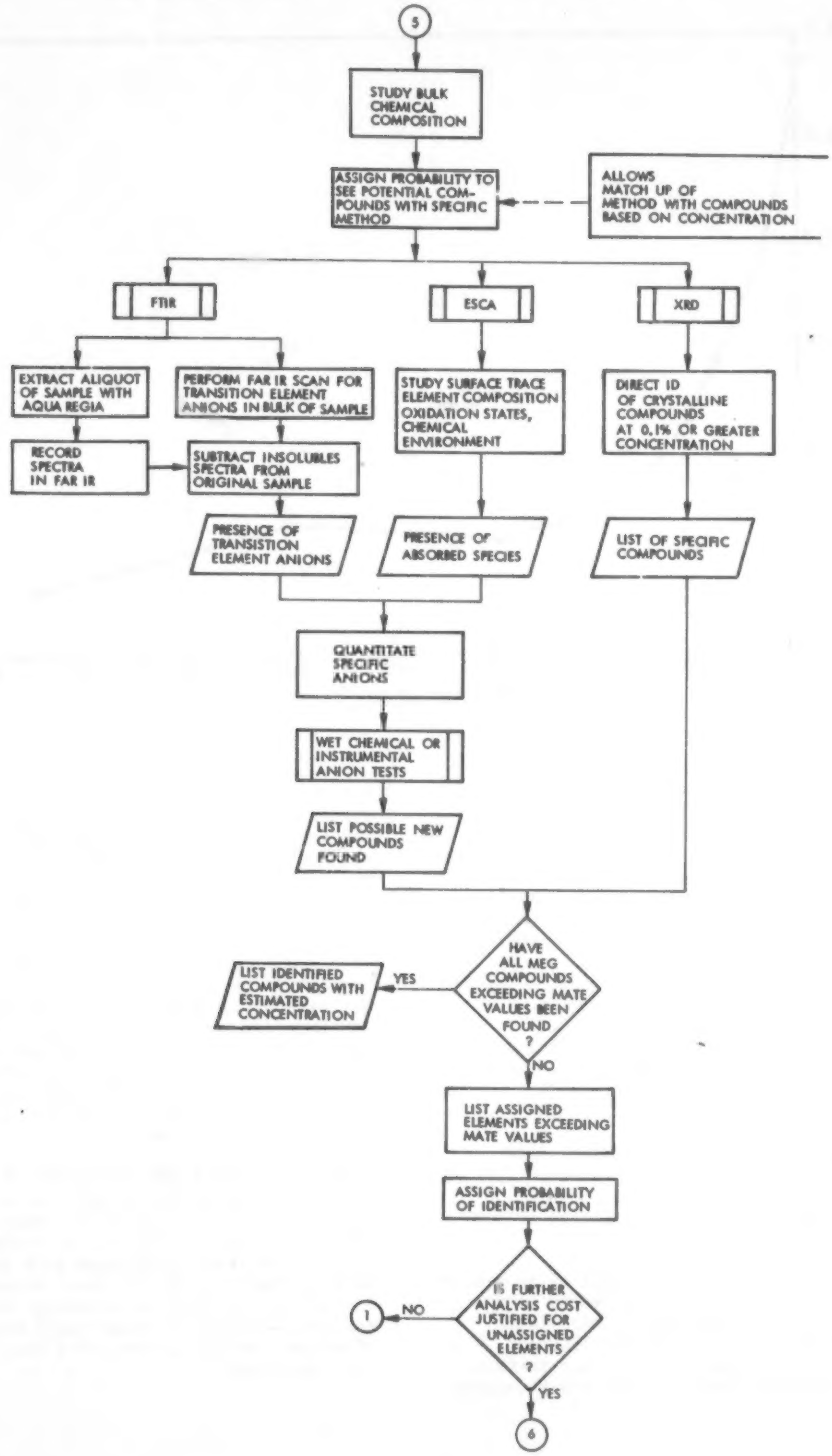
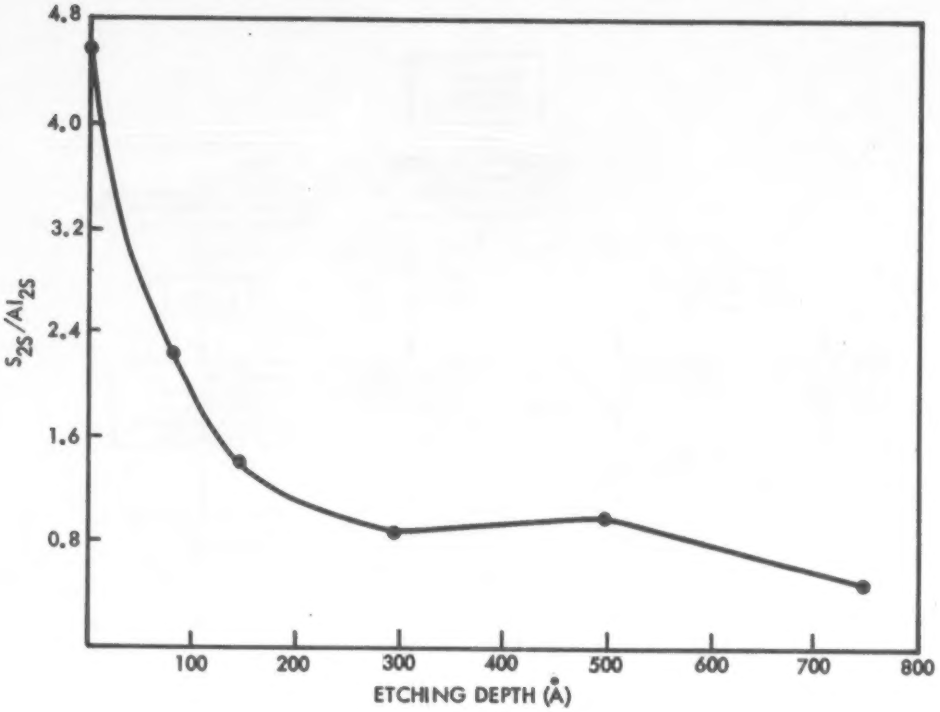

5
STUDY BULK CHEMICAL COMPOSITION
ASSIGN PROBABILITY TO SEE POTENTIAL COMPOUNDS WITH SPECIFIC METHOD
ALLOWS MATCH UP OF METHOD WITH COMPOUNDS BASED ON CONCENTRATION
FTIR
ESCA
XRD
EXTRACT ALIQUOT OF SAMPLE WITH AQUA REGIA
PERFORM FAR IR SCAN FOR TRANSITION ELEMENT ANIONS IN BULK OF SAMPLE
STUDY SURFACE TRACE ELEMENT COMPOSITION OXIDATION STATES, CHEMICAL ENVIRONMENT
DIRECT ID OF CRYSTALLINE COMPOUNDS AT 0.1% OR GREATER CONCENTRATION
RECORD SPECTRA IN FAR IR
SUBTRACT INSOLUBLES SPECTRA FROM ORIGINAL SAMPLE
PRESENCE OF TRANSISTION ELEMENT ANIONS
PRESENCE OF ABSORBED SPECIES
LIST OF SPECIFIC COMPOUNDS
QUANTITATE SPECIFIC ANIONS
WET CHEMICAL OR INSTRUMENTAL ANION TESTS
LIST POSSIBLE NEW COMPOUNDS FOUND
HAVE ALL MEG COMPOUNDS EXCEEDING MATE VALUES BEEN FOUND ?
YES
LIST IDENTIFIED COMPOUNDS WITH ESTIMATED CONCENTRATION
NO
LIST ASSIGNED ELEMENTS EXCEEDING MATE VALUES
ASSIGN PROBABILITY OF IDENTIFICATION
IS FURTHER ANALYSIS COST JUSTIFIED FOR UNASSIGNED ELEMENTS ?
NO
1
YES
6

FIGURE 8

SULFUR DEPENDENCE WITH ETCHING DEPTH FOR OUTLET COAL FIRED FILTER SAMPLE



Individual Particle Characterization. It should be emphasized that this phase of the analysis should be carried out at the analyst's discretion. The analyst should consider the sample, its source, the information already available, the type of information which is lacking, the instrumental techniques available, and analysis cost before proceeding.

Analytical techniques which are suggested for identification of individual particles include:

- Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM-EDX)
- Electron Probe Microanalysis (EPMA)
- Transmission Electron Microscopy with Selected Area Electron Diffraction (TEM-SAED)

The logic network for their application is summarized in Figure 9.

In SEM, the sample specimen is swept by an electron beam and the variation of the secondary electron emission intensity is recorded. This signal modulates the brightness of an oscilloscope beam, producing an image of the sample surface on the oscilloscope screen. Since the secondary electron beam is localized in the area impacted by the incident radiation, images of relatively high resolution are achieved which can provide morphological characteristics of individual particles. When SEM is used in conjunction with an energy dispersive X-ray spectrometer (EDX), the secondary X-rays produced can be monitored, thereby allowing identification and quantification of individual elements present in the sample. Determining the elemental distribution of a particle is particularly useful for those particles composed of various occluded materials, the high resolution and magnification of the SEM can produce images distinctive enough to identify the particle. As such, the SEM information is a valuable adjunct to the PLM, especially for particles smaller than 0.5μ.

Figure 10 shows a SEM photograph of a typical fly ash sample and as can be seen in the photograph there are areas for particles which appear to be growing on the surface of a particle that have a crystalline shape associated with them. Because we know that many of the trace elements found in fly ash can be found to a greater extent on the surface, analysis of these small microcrystalline structures on the surface of a large particle is very important.

FIGURE 9

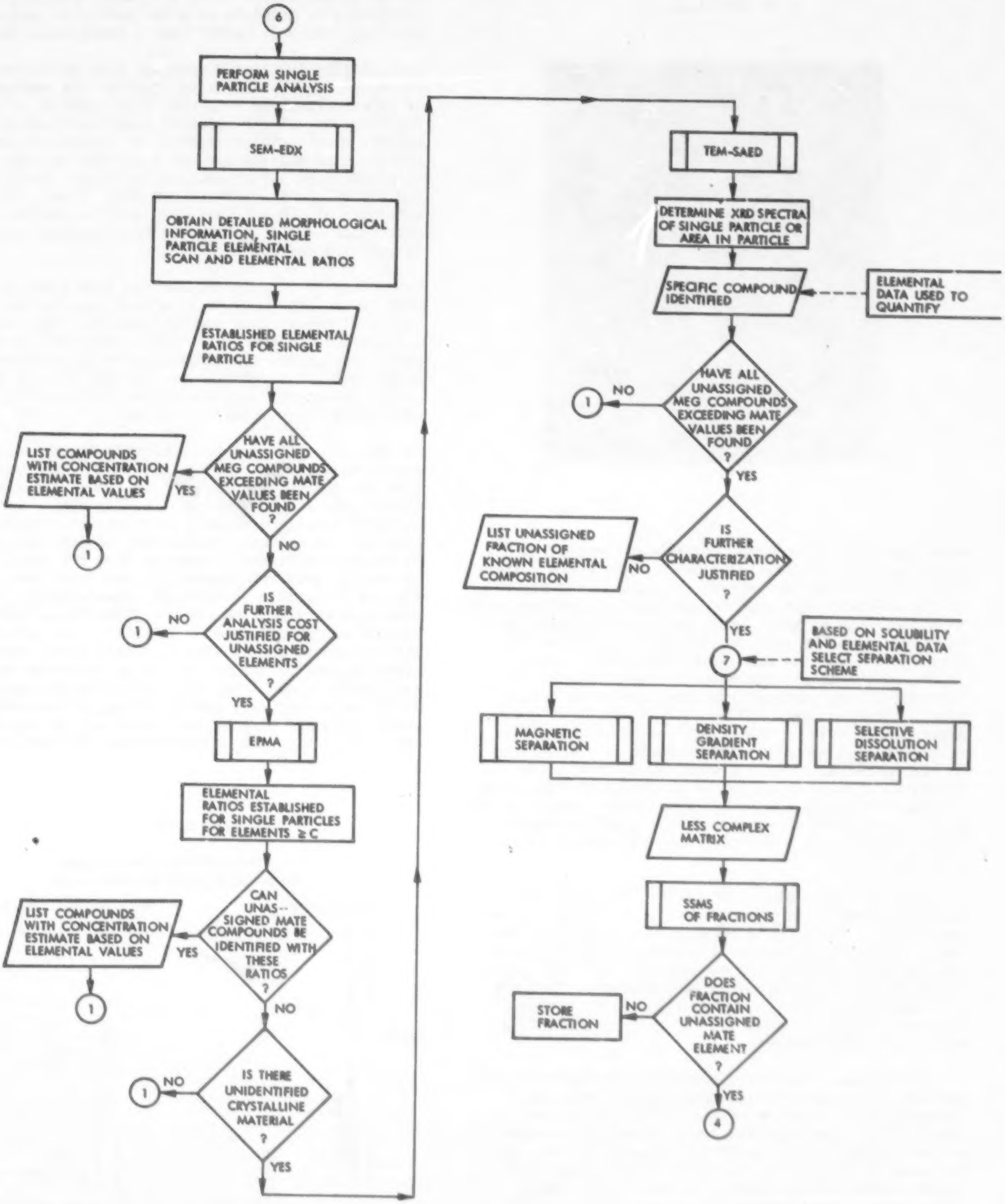
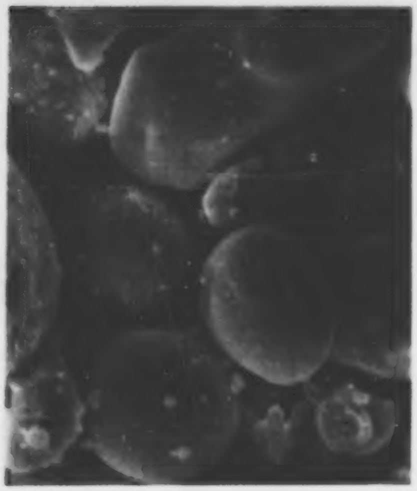

6
PERFORM SINGLE PARTICLE ANALYSIS
SEM-EDX
OBTAIN DETAILED MORPHOLOGICAL INFORMATION, SINGLE PARTICLE ELEMENTAL SCAN AND ELEMENTAL RATIOS
ESTABLISHED ELEMENTAL RATIOS FOR SINGLE PARTICLE
HAVE ALL UNASSIGNED MEG COMPOUNDS EXCEEDING MATE VALUES BEEN FOUND ?
YES
LIST COMPOUNDS WITH CONCENTRATION ESTIMATE BASED ON ELEMENTAL VALUES
1
NO
IS FURTHER ANALYSIS COST JUSTIFIED FOR UNASSIGNED ELEMENTS ?
NO
1
YES
EPMA
ELEMENTAL RATIOS ESTABLISHED FOR SINGLE PARTICLES FOR ELEMENTS ≥ C
CAN UNAS-- SIGNED MATE COMPOUNDS BE IDENTIFIED WITH THESE RATIOS ?
YES
LIST COMPOUNDS WITH CONCENTRATION ESTIMATE BASED ON ELEMENTAL VALUES
1
NO
IS THERE UNIDENTIFIED CRYSTALLINE MATERIAL ?
NO
1
YES
TEM-SAED
DETERMINE XRD SPECTRA OF SINGLE PARTICLE OR AREA IN PARTICLE
SPECIFIC COMPOUND IDENTIFIED
ELEMENTAL DATA USED TO QUANTIFY
HAVE ALL UNASSIGNED MEG COMPOUNDS EXCEEDING MATE VALUES BEEN FOUND ?
NO
1
YES
IS FURTHER CHARACTERIZATION JUSTIFIED ?
NO
LIST UNASSIGNED FRACTION OF KNOWN ELEMENTAL COMPOSITION
YES
7
BASED ON SOLUBILITY AND ELEMENTAL DATA SELECT SEPARATION SCHEME
MAGNETIC SEPARATION
DENSITY GRADIENT SEPARATION
SELECTIVE DISSOLUTION SEPARATION
LESS COMPLEX MATRIX
SSMS OF FRACTIONS
DOES FRACTION CONTAIN UNASSIGNED MATE ELEMENT ?
NO
STORE FRACTION
YES
4

FIGURE 10

SEM PHOTOGRAPH OF COAL FLYASH SHOWING
CRYSTALLINE MATERIAL ON SURFACE
OF PARTICLES



An alternative to scanning electron microscopy is Scanning Auger Microanalysis which might prove in the future to be a better method. Because of the power of the electron beam used in SEM, surface analysis can be difficult. In many cases, surface structures on a particle cannot be analyzed for their elemental composition because the beam penetrates to the surface of the particle, and consequently the elemental composition of the surface structures cannot be determined. However, with SAM the surface capability of Auger can be used to specifically determine the elemental composition of microstructures on the surface of the particle. At the present time because the lowest resolution is on the order of 0.2 microns, many of the more interesting microcrystalline structures on a particle cannot be seen to be analyzed thoroughly, but this limitation is expected to be removed in the near future.

In order to reduce the mounting time for both SEM and EPMA (electron probe microanalysis), particles can be mounted on a sticky gold to provide a conductive surface. Normally, a carbon film would be deposited on the sample to ensure its conductivity. If the sample is reasonably conductive and long analysis times are not necessary, then the carbon film may be omitted. Mounting samples in this fashion will not interfere with later EPMA analysis.

In EPMA, a small energetic electron beam impinges the surface of the particulate specimen and produces characteristic X-ray emissions. EPMA can be used to qualitatively and quantitatively determine the elemental composition of particles ranging in size from 20μ down to about 0.2μ, for most of the elements of atomic numbers above that of carbon. Instruments using wavelength dispersive X-ray spectrometers can resolve spectra of elements sulfur through nickel in atomic number. Peak heights, or intensity ratios, are measured on samples and standards to provide a quantitative analysis. To achieve the best accuracy, it is necessary to do a considerable amount of sample preparation. In most cases it is necessary to have standards similar in particle size and composition to the sample being analyzed. Further, identification is possible only for particles containing discrete compounds rather than a homogeneous mixture.

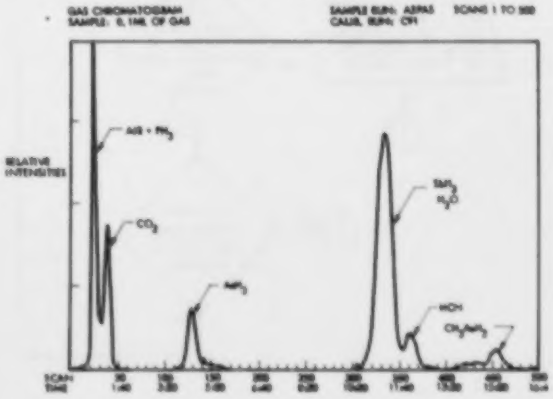
Transmission Electron Microscopy with Selective Area Diffraction (TEM-SAED) also involves the impingement of an electron beam on a thin film (1500 A) of sample. The resulting single particle X-ray diffraction pattern permits identification of crystallin compounds. The qualitative and quantitative data obtained is excellent because individual particles and fibers can be observed and identified. This attribute of TEM-SAED has been used to provide dependable identifications of such chemical species as asbestos and silica.

Combining the information derived from TEM-SAED and EPMA can aid the analyst in assembling the total nature of the various species present. Many substances which appear essentially identical in elemental composition as measured with the electron probe, will be determined by TEM-SAED to have a unique morphology and, therefore, their emitted nature and source clearly indicated.

At this point, if all the compounds for MEG elements exceeding their MATE values have not been found, then the analyst might choose to reduce the sample matrix into simple mixtures. He can either run magnetic density gradient, or selective dissolution studies. In magnetic separation, magnets are used to remove the magnetic fraction from the sample. In density gradient separation, particles are floated in organic solvents of known density. Considerable care must be used in selecting solvents, because compounds could be soluble in the solvents. This procedure can be used to obtain gross separations by density or can be used to determine individual particle densities for identification purpose. Selective dissolution uses a variety of solvents to remove more and more of the sample and in the process simplifying the composition of the residue.

FIGURE 11

GAS CHROMATOGRAM OF HYDRIDE PRODUCED BY REDUCTION PROCEDURE



In all these separation techniques care must be taken to avoid contamination and scrambling of compounds. Also, reasonably large quantities of sample are necessary. The end result of these separations is to provide less complex fractions which can be studied starting at the bulk characterization level.

Liquid Samples. These previous techniques which have been talked about are primarily used for solid samples and are noramlly not applied to liquid samples. In the case of the liquid samples we are not normally dealing with true compounds. In all cases we can derive information on the cations and anions present with a high level of accuracy; determine the oxidation states such as Fe^{+2}/Fe^{+3}, or As^{+3}/As^{+5}; or analyze for organimetallics. Figure 10 shows a technique that was developed in the labs at TRW to analyze for various organometallics that might be present in a sample. The procedure combines chemical reduction with the operations, and identification, and quantitatives capabilities of GC/MS. The samples were treated to evolve the hydrides, which were trapped in LN_2. The trapped hydrides are then injected into the GC/MS for analysis. This technique has shown great utility and has been applied to samples from an oil shale gasifier with good success.

Summary. The Level 2 analysis procedures do have several problems associated with them. The main problem Level 2 analysis is the analysis gap between the capability to measure major versus minor constituents of the sample. X-ray diffraction which is the only true compound identification technique for inorganic analysis, yet it requires samples to contain on the order of 0.1 percent or better of the compound to be identified. Trace compounds at the ppm level are difficult if not impossible to identify unambiguously with the present capabilities. Presented are a series of logic charts to guide the analyst through a Level 2 procedure. However, since Level 2 is a more sophisticated approach to the analysis of an inorganic sample, it will require a trained analyst to interpret the data and to direct the research. It is not envisioned to provide a prescribed set of specific procedures but to provide an overall general approach to the analyst. Since there is no one analytical technique that can identify all inorganic compounds, most samples will require an integrated approach using a variety of methods.

In the future, it will be necessary to develop recording formats for both Level 1 and Level 2 inorganic analysis results and to develop more definitive criteria that will control the decision to proceed from Level 1 to Level 2.

More work is necessary to apply these techniques to environmental samples which tend to be more complex and difficult than routine samples normally seen by the techniques. When these problems are met, a specific set of procedures can then be developed to cover the potential problems which an analyst might find for Level 2 analysis.

References.

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[2] Hamersma, J.W. and Reynolds, S.L., "Field Test Sampling/Analytical Strategies and Implementation Cost Estimates: Coal Gasification and Flue Gas Desulfurization," EPA-600/2-76-093b, U.S. Environmental Protection Agency, Research Triangle Park, N.C., April 1976

[3] Cleland, J.G., and Kingsbury, G.L., "Multimedia Environmental Goals for Environmental Assessment Volumes 1 and 2", EPA 600/7-77-136a and b, U.S. Environmental Protection Agency, Research Triangle Park, November 1977.

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[5] Jenkins, R., Haas, D.J. and Paoline, F.R. Norelco Reporter, 18 (2), 1 (1971).

Organic Analysis for Environmental Assessment

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Abstract

Systematic measurement methods are being developed for the determination of organic species in emission and process streams. The methods are structured on the Phased approach developed by the Process Measurements Branch of IERL/RTP. Level 1 analysis methods have been tested and a reporting format developed which is consistent with a variety of assessment objectives. Level 2 procedures are focused on general broad spectrum analysis protocols and specific analyte procedures such as for PCB's, PAH, etc.

Introduction

Chemical analysis for environmental assessment is currently based upon the Phased Approach established by the Process Measurements Branch of EPA/IERL/RTP.(1) The purpose of this paper is a review of the status and procedures for Level 1 and Level 2 organic analysis, with a focus on changes in the Level 1 procedures originally proposed, the development of a consistent reporting format and various activities in the development of Level 2 organic analysis procedures.

Level 1 Organic Analysis Procedures

The Level 1 sampling and analysis procedures are described in detail in the EPA Level 1 Procedures Manual(2) and will not be discussed in detail in this paper. Some highlights of the procedures and areas where changes have been made to improve the accuracy of the data will be reviewed.

Streams to be sampled for environmental assessment include process and effluent streams which may be gaseous, liquid or solid and which are sampled by a variety of methods. Grab sampling procedures are used for most of the liquid and solid samples. The most complex sampling is that of the gaseous stream which involves the use of gas sampling for on-site analysis and vapor and particulate sampling with the SASS (Source Assessment Sampling System) train. The Grab and SASS samples are returned to the laboratory for analysis. A summary of the types of samples generated for analysis is shown in the overview given in Figure 1.

This overview shows that the organic analyses are either done directly on the gas samples (materials with a boiling point less than 110°C) and neat organic liquids, such as fuels, or on methylene chloride extracts of the samples or portions of the SASS train. In the case of rinses from the SASS train, such as the sorbent module rinse, it is necessary to evaporate the rinses to dryness before proceeding with the analysis, because the alcohol used in the rinsing will interfere with the liquid chromatography step of the analysis. Care is taken in handling of these liquids and solutions to recognize that many of the materials of interest are volatile (boiling point 100 - 300°C) and will be lost if samples are taken to dryness.

The overall Level 1 analysis scheme for the organic components is shown in Figure 2. The procedure covers the quantitative analysis of the major volatility classes by the procedures indicated below:

Volatility	Definition		Procedure
gases	boiling point	< 100°C	field GC
volatile	boiling point	100-300°C	TCO
non-volatile	boiling point	> 300°C	GRAV

The TCO procedures is a laboratory gas chromatographic (GC) method for the volatile components. The GRAV procedure is a gravimetric method for the non-volatile components.

The major chemical categories in each sample are determined by first separating the sample according to polarity on a silica gel liquid chromatography (LC) column. Each of the fractions are then identified by obtaining infrared (IR) and low resolution mass spectral (LRMS) data.

Reporting Level 1 Analysis Results

The first complete set of data to be developed in the Level 1 organic analysis are the LC results which are reported in the form shown in Table 1. The volatile (TCO) and non-volatile (GRAV) components of each LC fraction are reported after computing back to equivalent quantities in the entire sample. The total quantity of each fraction is then derived from the sum of TCO + GRAV and the concentration in the sampled stream is calculated from the sample quantity and volume sampled.

Results of the IR analysis of each sample and LC fraction are tabulated in terms of the frequency of peak maxima, intensity (weak, medium or strong) and probable assignment. A typical example is given in Table 2.

The LRMS results are reported in terms of the criteria outlined in Table 3. A typical report using this format is shown in Table 4. Most of the subsequent initial Level 1 interpretation of data is done using only the major compound category data. Compound categories for LRMS interpretation are chosen primarily from a list of about twenty-four general compound groupings.

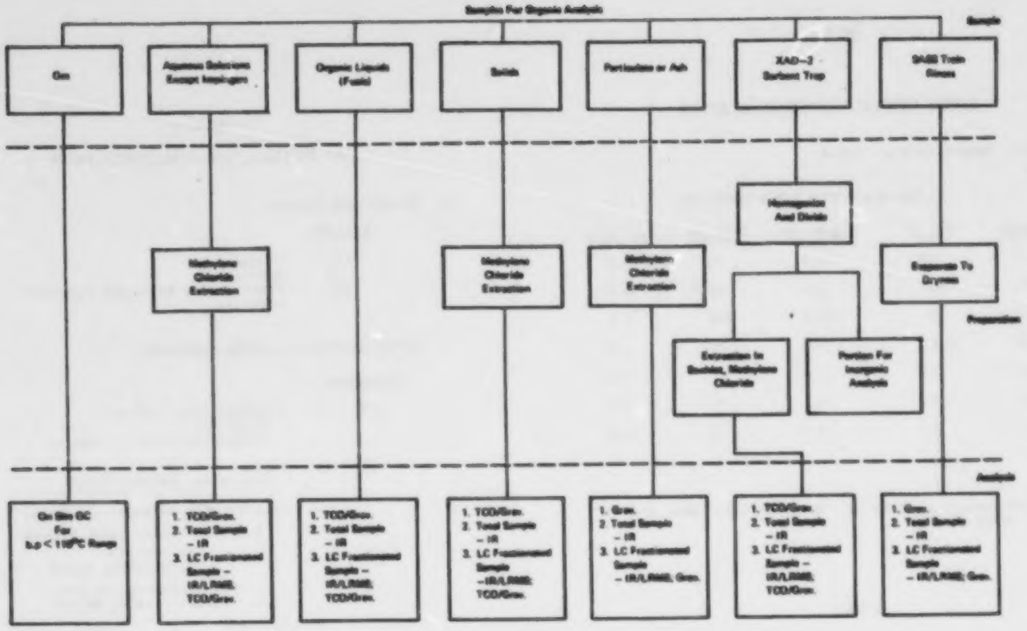

Samples For Organic Analysis
Sample
Gas
Aqueous Solutions Except Impingers
Organic Liquids (Fuels)
Solids
Particulates or Ash
XAD–2 Sorbent Trap
SASS Train Rinses
Homogenize And Divide
Methylene Chloride Extraction
Methylene Chloride Extraction
Methylene Chloride Extraction
Evaporate To Dryness
Preparation
Extraction In Soxhlet, Methylene Chloride
Portion For Inorganic Analysis
Analysis
On Site GC For b.p < 110°C Range
1. TCO/Grav. 2. Total Sample – IR 3. LC Fractionated Sample – IR/LRMS; TCO/Grav.
1. TCO/Grav. 2. Total Sample – IR 3. LC Fractionated Sample – IR/LRMS; TCO/Grav.
1. TCO/Grav. 2. Total Sample – IR 3. LC Fractionated Sample – IR/LRMS; TCO/Grav.
1. Grav. 2. Total Sample – IR 3. LC Fractionated Sample – IR/LRMS; Grav.
1. TCO/Grav. 2. Total Sample – IR 3. LC Fractionated Sample – IR/LRMS; TCO/Grav.
1. Grav. 2. Total Sample – IR 3. LC Fractionated Sample – IR/LRMS; Grav.

Figure 1: MULTIMEDIA ORGANIC ANALYSIS OVERVIEW

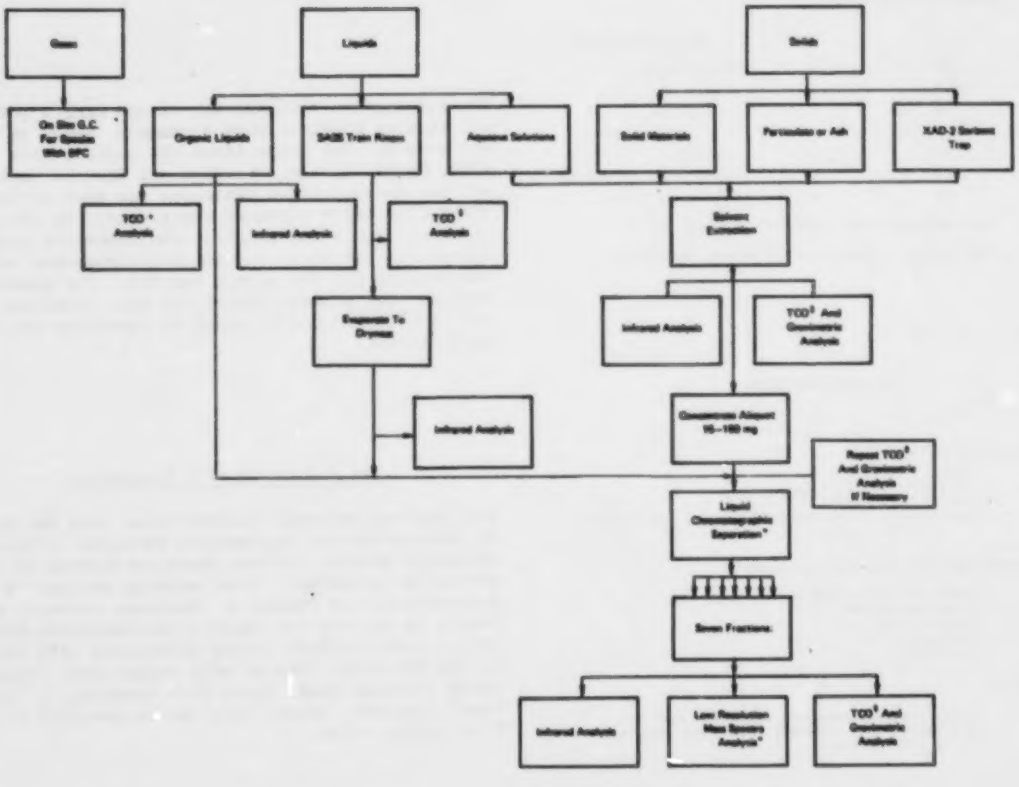

Gases
Liquids
Solids
On Site G.C. For Species With BPC
Organic Liquids
SASS Train Rinses
Aqueous Solutions
Solid Materials
Particulates or Ash
XAD-2 Sorbent Trap
TCO Analysis
Infrared Analysis
TCO Analysis
Solvent Extraction
Evaporate To Dryness
Infrared Analysis
TCO And Gravimetric Analysis
Infrared Analysis
Concentrate Aliquot 10–100 mg
Repeat TCO And Gravimetric Analysis If Necessary
Liquid Chromatographic Separation
Seven Fractions
Infrared Analysis
Low Resolution Mass Spectra Analysis
TCO And Gravimetric Analysis

FIGURE 2 LEVEL I ORGANIC ANALYSIS FLOW DIAGRAM

Table 1

Example Report of LC Fractionation Results

Sample: Sorbent Extract - SASS 4

Equivalent Total Sample Quantities

Fraction	TCO, mg	GRAV, mg	Total, Mg	Total mg/m³
LC1	5.2	12.5	18.	0.46
LC2	19.	3.3	22.	0.56
LC3	73.	182.0	260.	6.6
LC4	6.7	23.3	30.	0.76
LC5	3.7	7.3	11.	0.28
LC6	5.3	40.7	46.	1.2
LC7	0.1	14.7	15.	0.38

Quantity actually taken for LC: 42 mg TCO; 103 mg GRAV, 3/10 of total sample extract.

Table 2

IR Report

Coal Extract - LC Fraction 6

1. Major peaks and assignments

ν, cm^{-1}	I	Assignments/comments
3300	m	OH or NH/broad
3080-3000	w	aromatic CH
2950, 2925, 2850	s	aliphatic CH
1690, 1650, 1600	m	acid, ketone or amine
1450	m	aliphatic
1200	w	ether, ester, or alcohol
750	m	substituted benzene

2. Unassigned weak bands: 1270, 1275, 870, 810, 660 cm^{-1}

3. Other remarks: Cannot confirm phthalates found by LRMS

Table 3

LRMS Report Format

1. Categories Present
    - Name
    - Molecular Weight Range
    - Composition Range
    - Approximate Intensity (100 = major, 10 = minor, 1 = trace)
2. Subcategories, Specific Compounds
    - Names of categories or subcategories
    - Molecular weight
    - Composition
    - Assignment
    - Intensity
3. Other
    - Other observed apparent molecular ions or significant ion clusters which were unable to be interpreted.

Table 4

LRMS Report - Coke Oven Quench Waste

1. Categories Present

Intensity	
100	Phenols
1	Amines
100	Heterocyclic nitrogen compounds
1	Nitriles

2. Subcategories, Specific Compounds

Intensity	
100	a. Phenols, alkyl series MW 94-122 Composition C_6H_6O - $C_8H_{10}O$
1	b. Amines Toluamine, MW 107, C_7H_9N
	c. Heterocyclic Nitrogen Compounds
100	1. Quinolines, alkyl series MW 129-157 Composition C_9H_7N - $C_{11}H_{11}N$
1	2. An imidazole, MW 174
1	3. Benzothiazole, MW 135
	d. Nitriles
1	Tolunitrile, MW 117, C_8H_7N

3. OTHER

1	Isotope cluster at 95, 96, 97, 98, 99
10	m/e 119

The information from the LC, IR and LRMS reports may then be combined into a summary report as shown in Table 5. The table lists the quantitative data (TCO, GRAV) for each fraction and for the total, and the concentration estimates for each of the identified major compound categories. In the case of liquid and solid samples, the summation column represents the total concentration/compound category information for the stream sampled. For gaseous streams, the summary report for each component of the SASS train must be added to determine the stream composition.

Level 1 to Level 2 Transition

The chemical category concentration data may be used to compare against appropriate decision criteria to determine whether further characterization or other action is warranted. This decision process is shown schematically in Figure 3. Relevant criteria currently in use are the Level 1 concentration limit of 0.5 mg/m or MATE values associated with compounds in the MEG list. Use of MATE values will require using the most toxic value in a category, a "worst case" approach, unless data can be provided to justify a higher value.

Table 5

Example Organic Extract Summary Table for a Sorbent Module Extract

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total organics, mg/m^3	0.61	0.74	8.4	1.0	0.33	1.5	0.50	13.
TCO, mg	5.2	19.	73.	6.7	3.7	5.3	0.1	110
GRAV, mg	13.	3.3	180.	23.	7.3	41.	15.	280
Categories	INT/mg/m^3							mg/m^3
Sulfur	100/0.6							0.6
Aliphatic HC's	10/0.06							0.06
Aromatics-Benzenes		10/0.06						0.06
Fused Arom <216		100/0.6	100/4	100/0.5				5.
Fused Arom >216		10/0.06	100/4	100/0.5				5.
Heterocyclic S		10/0.06	10/0.4	10/0.05				0.5
Heterocyclic N				10/0.05	/0.1*	100/0.7	10/0.02	1.
Heterocyclic O					/0.01*	10/0.07	100/0.2	0.3
Carboxylic Acids					/0.1*	100/0.7	100/0.2	1.0
Phenols					/0.01*	10/0.07	10/0.02	0.1
Esters					/0.01*	10/0.07		0.08

* Estimated assuming same relative intensities as LC6, since IR spectra of LC5 and LC6 very similar.

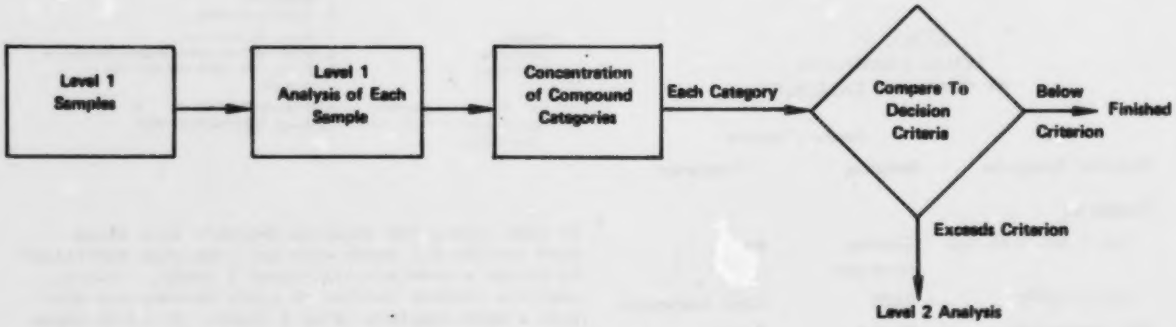

Level 1 Samples
Level 1 Analysis of Each Sample
Concentration of Compound Categories
Each Category
Compare To Decision Criteria
Below Criterion
Finished
Exceeds Criterion
Level 2 Analysis

Figure 3: DECISION LOGIC FOR PHASED LEVEL 1 – LEVEL 2 ANALYSIS

Level 2 Sampling and Analysis Activities

The Level 2 methods for organic analysis are currently in the development stage and cover a wide range of possibilities. Level 2 procedures include the analysis of specific compounds tentatively identified in the Level 1 study, more comprehensive sampling and analysis schemes and the development of procedures for specific purposes such as PCB and PAH analysis and on-site extractive water sampling.

Level 2 Sampling

Most of the sampling procedures chosen for Level 1 were the best available and are still appropriate for Level 2 studies. Some procedures will need improvement, while some might be made simpler or more specific. Examples of additional sampling procedures which could be used in Level 2 are listed below:

Phase	Method
Gases	- Bags, impingers
Vapors	- Sorbents, Modified 5, Impingers
Particulates	- Method 5, Special
Liquids	- Continuous (XAD-2), Purge & Trap
Solids	- Stop Belt, Cutter

An interim Level 2 Procedures Manual has been drafted and will be published in Feburary, 1978. This manual explains each of these methods in greater detail and gives specific recommendations for certain categories of compounds as is shown in Table 6.

Table 6

LEVEL 2 SAMPLING
BY CHEMICAL CATEGORY

	Gaseous Streams	
Chemical Categories	Sampling	Treatment
Aldehydes		
b.p. < 100°C (< C_5)	Bisulfite Impingers	None
b.p. > 100°C	SASS	Resin Adsorption
Azo Compounds, Hydrazine, Etc.	Special Reagent Impingers	None
Fused Polycyclic Hydrocarbons Fused Non-Alternant Polycyclic Hydrocarbons	SASS	Resin Adsorption

Level 2 Analysis

Chemical analysis following Level 1 studies will focus largely on more accurate specific compound identification. To this end several procedures should be considered in addition to those used in the Level 1 studies. Some key techniques are:

Thermal Analysis (TGA)
Gel Permeation Chromatography (GPC)

High Performance Liquid Chromatography (HPLC)

High Resolution Mass Spectrometry (HRMS)
Gas Chromatography/Mass Spectrometry (GC/MS)

Nuclear Magnetic Resonance (NMR)
Ultraviolet Spectroscopy (UV)

The objective in adding these procedures is to deal better with the high molecular weight species (TGA, GPC), further resolve complex fractions (HPLC) from the LC separation and provide more complete and/or specific analysis capabilities (HRMS, GC/MS, NMR, UV).

Examples of recommended analysis methods for specific compound categories given in the interim Level 2 manual are shown in Table 7.

Table 7

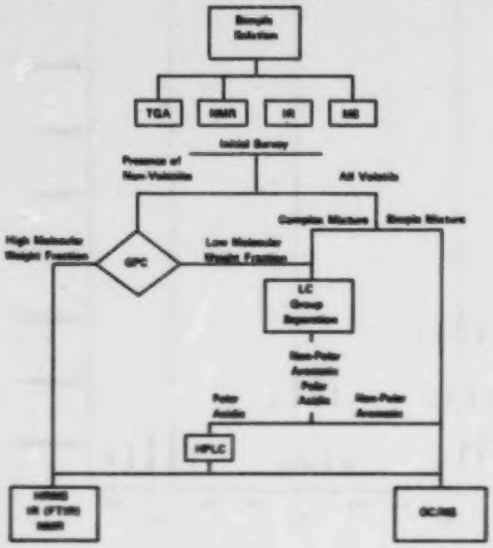
LEVEL 2 ANALYSIS
BY CHEMICAL CATEGORY

Chemical Category/Subcategory	Analysis Method
Alkyl Halides	
b.p. < 100°C	GC/MS or GC/ECD (Isothermal) on Porapak Q
b.p. > 100°C	GC/MS or GC/ECD (Isothermal) on SP-2250 (or OV-17)
Aldehydes	1. Iodometric Titration of Bisulfite Impingers or 2. GC/MS on SP-1000
Phenols Halophenols Nitrophenols	1. Reverse Phase HPLC or 2. GC/MS on Tenax (Direct Aqueous Injection) or 3. GC/MS on SP-1000 After Derivative Formation
Fused Polycyclic Hydrocarbons Fused Non-Alternant Polycyclic Hydrocarbons	1. GC/MS on Dexsil 400 or 2. Reverse or Normal Phase HPLC

In some cases, the chemical analysis data alone from the Level 1 study will not have been sufficient to direct a more specific Level 2 study. However, positive biotest results or other reasons may dictate a more complete Level 2 study. To cover these cases, a general comprehensive Level 2 analysis scheme is envisaged as shown in Figure 4. This scheme utilizes the additional methods mentioned earlier to search for high molecular weight materials and also recognizes the need to resolve the complex LC fractions by HPLC prior to analysis. The best available specific analysis techniques are used to determine the composition of the sample, including those components present at low concentration levels.

Figure 4

GENERAL LEVEL 2 SCHEME FOR SOLUTIONS OF SAMPLE EXTRACTIONS



Other Level 2 Related Activities

Several other studies are in progress in the Arthur D. Little, Inc. laboratories related to more specific Level 2 studies and the development of alternate procedures. Some of these studies are:

- The development of specific PCB and PAH procedures using GC/MS
- Studies of the application of HRMS
- Evaluation of gas sampling using multilayer bags and
- Design of a continuous on-site extractive sampler for water based upon combined resin systems.

The PCB and HRMS studies are described briefly in this paper.

Polychlorinated Biphenyl (PCB) Procedure

Most of the current procedures for PCB analysis rely upon recognition of the typical chromatographic profile to identify the specific PCB (or Arclor) and quantitation by some combination of peak height measurement and calibration. This procedure breaks down for combustion sources due to preferential combustion of the lower chlorinated biphenyls, resulting in distorted GC profiles. This problem has been overcome by using GC/MS procedures and selected mass scanning. The basic procedure is to measure separately the monochloro, dichloro, ——— etc. chlorinated biphenyls. Hypothetical mass spectra for each of the chlorinated biphenyls is shown in Figure 5. This figure shows that a specific mass may be chosen to measure each n chlorinated biphenyl group with minimum interference from the others. There is no interference between groups separated by one chlorine atom. For those separated by two chlorine atoms there is mass spectral interference, but there is no chromatographic overlap between the groups. These two factors can be combined as shown in Figure 6 to provide relative retention time (RRT) windows at selected masses for the specific measurement of a particular chlorinated biphenyl group.

Using this procedure, the results shown below were obtained on a sample whose composition was known from previous detailed GC studies.

PCB Group	Found by GC/MS	Known
Cl_1	0	0
Cl_2	2	1.2
Cl_3	26	24.7
Cl_4	55	57.8
Cl_5	17	19.8
Cl_6	0	0.4

High Resolution Mass Spectrometry (HRMS) Matrix Analysis

The complete analysis of a sample is done best when there is some initial knowledge of the sample composition and, therefore, an appreciation of special precautions or procedures that should be used. In environmental assessment studies, the analyst is all too often hampered by lack of any knowledge of the sample chemistry.

High resolution mass spectrometry (HRMS) provides a basis from which one can obtain a complete overview of the probable sample composition. The HRMS matrix approach is intended to present a quick, relatively inexpensive overview of a sample's composition to guide further analysis.

The HRMS matrix method consists of a series of computer programs which sort and file the data from a high resolution mass spectrum. A typical HRMS may consist of 400 - 1000 spectral lines and associated composition data. The type of data available is shown in Table 8 for the three different composition peaks observed at m/e 196. Listed are the peak intensity (HGT), exact mass (DET MASS), difference in exact mass (ERROR) between the observed mass and that computed for the composition given, the "rings plus double bonds" (R+DB) value and the composition in terms of the number of atoms of the element listed.

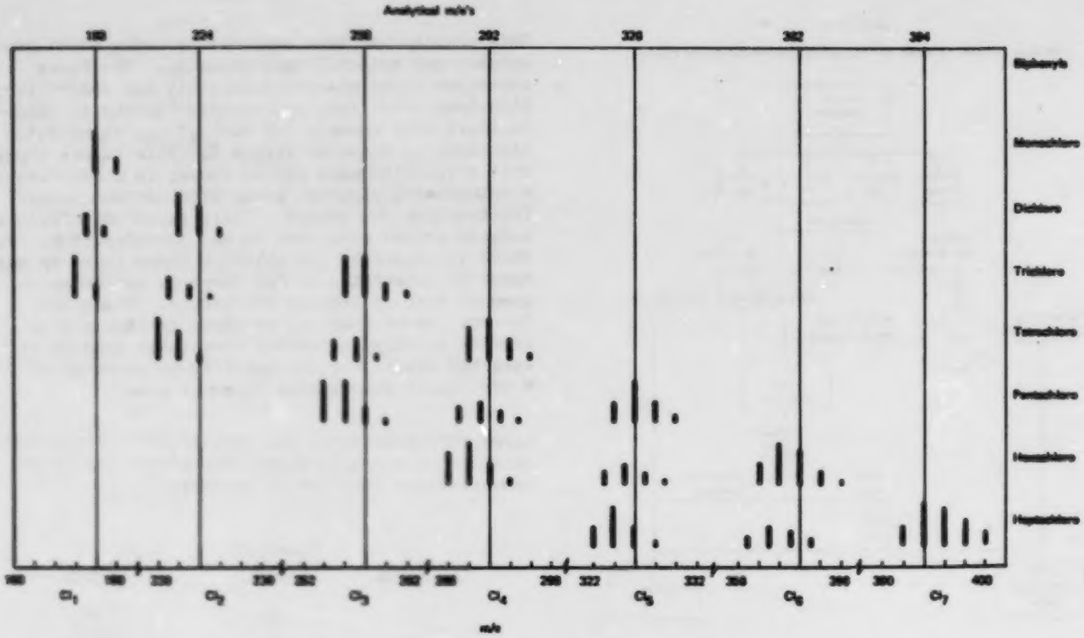


Figure 5: HYPOTHETICAL MASS SPECTRA OF PCB's

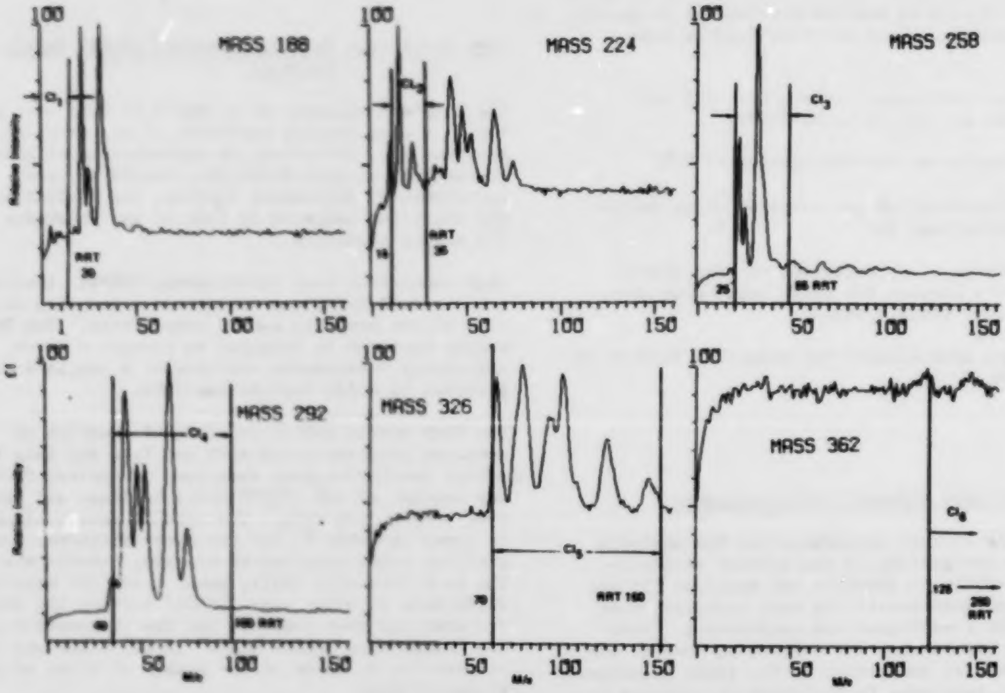


Figure 6: ANALYTICAL MASS CHROMATOGRAMS FOR AN AROCLOR 1248 SAMPLE

Table 8
Example of HRMS Data

— Observed —		——— Calculated ———						
HGT	DET. MASS	ERROR	R+DB	C	H	N	O	S
19	196.08886	0.04	9.0	14	12	0	1	0
95	196.12577	0.57	8.0	15	16	0	0	0
35	196.21963	0.53	1.0	14	28	0	0	0

The R+DB value is a measure of hydrogen (H_2) unsaturation in the molecule and is a convenient index of structural type. The R+DB value is computed from the formula

$$R{+}DB = 1.0 + n_C - 0.5\, n_H + \sum k_i n_i$$

where k values for some key elements are

N	0.5
O	0.0
S	0.0
Cl	- 0.5

The R+DB value computed for some polynuclear aromatic hydrocarbons is given in Table 9.

Table 9
R+DB Values for Polynuclear Aromatic Hydrocarbons

R+DB	MW[*]	Composition[*]	Compound[**]
9	166	$C_{13}H_{10}$	Fluorene
10	178	$C_{14}H_{10}$	Anthracene
11	204	$C_{16}H_{12}$	Aceanthrylene
12	202	$C_{16}H_{10}$	Pyrene
13	228	$C_{18}H_{12}$	Chrysene
15	252	$C_{20}H_{12}$	Benzopyrene

[*] lowest possible value in R+DB group

[**] and related isomers

Through a combination of the R+DB value and the chemical composition assignments, the entire HRMS output may be described as a simplified matrix of data, such as shown in Table 10 for a solvent extract of an API separator waste.

Table 10
R+DB Matrix: API Waste Extract[*]

Relative Abundance by Composition

R+DB	CH (only)	CH+N	CH+O	CH+S
0	5.9	0.0	0.0	0.0
1	13.6	0.0	0.0	0.0
2	8.4	0.0	0.0	0.0
3	5.4	0.0	0.0	0.0
4	8.9	0.0	0.0	0.3
5	4.7	0.0	0.0	0.0
6	4.8	0.0	0.0	0.2
7	19.4	0.0	0.0	0.0
8	8.2	0.0	0.0	0.0
9	4.6	0.0	0.6	0.9
10	5.7	0.0	0.0	0.0
11	1.1	0.0	0.0	0.0
12	0.1	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0
14	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0

[*] numerical values in matrix given as % of total

Examination of the HRMS R+DB matrix of this sample reveals that there are no nitrogen-containing species (R+DB 9) and three types of sulfur species (R+DB 4, 6 and 9) all at low levels. The sample is mostly hydrocarbons, predominantly aromatic, with no detectable species above pyrene (R+DB 12). Further examination of the subset data used to prepare the final matrix reveals that the R+DB 9 oxygen and sulfur species are benzothiophene (R+DB 6) and a series of thiophenols (R+DB 4).

Information derived from this type of matrix analysis can be of great value in establishing criteria for the full analysis.

Further information concerning the material presented in this paper may be obtained by contacting the author or the EPA Project Officer, Dr. Larry D. Johnson, Process Measurements Branch, IERL/EPA/RTP. The work described in this paper has been conducted under EPA Contract No. 68-02-2150.

References

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A CRITIQUE OF ORGANIC LEVEL-1 ANALYSIS

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Abstract

This paper provides an objective review of organic Level-1 analysis. It attempts to point out present strengths and weaknesses, and to make recommendations concerning how improvements may be made. Areas which are addressed include the adequacy of sample size, the optimum LC separation scheme, problems associated with contamination both in the field and as a result of adsorbent degradation, the utility of FT-IR, and LRMS analysis.

Introduction

It is important to remember that the evolution of Level-1 was intended, it was supposed to happen. There was never any pretence that the first drafts, prepared two years ago, would be used without modification. The most recent update is presently (February 1978) being assembled by Research Triangle Institute.

This brief review will not attempt to cover all aspects of organic Level-1 analysis, rather, it will discuss selected aspects of analysis of the organic Level-1 liquid chromatographic fractions.

Analysis of LC Fractions

The most straightforward way to address the analysis of the LC fractions in organic Level-1 analysis is to consider each fraction in turn, and discuss typical strengths and weaknesses as appropriate. We have thus chosen to examine a typical sample from FBC coal combustion effluent, and will add other examples by way of illustration as necessary.

Fraction 1

We do not normally expect to see anything in Fraction 1, above normal background, and Figure 1 shows a typical Fraction 1 spectrum. All peaks in this case were attributed to background contamination.

However, appreciable contamination from silicone grease is occasionally evident in Fraction 1, as illustrated in Figure 2. It is apparent that such spectra arise when silicone grease is used in any part of the heated sampling train. Since such strong absorbance would render further IR interpretation either difficult or impossible, it is recommended that the use of silicone grease should be discontinued. Besides interferring with qualitative interpretation, the gravimetric measurements would also be rendered meaningless by the presence of such contaminants.

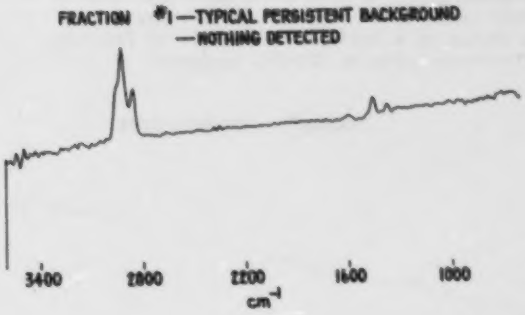

FIGURE 1. EXXON 1601-1
(Level-1 IR, m=10)

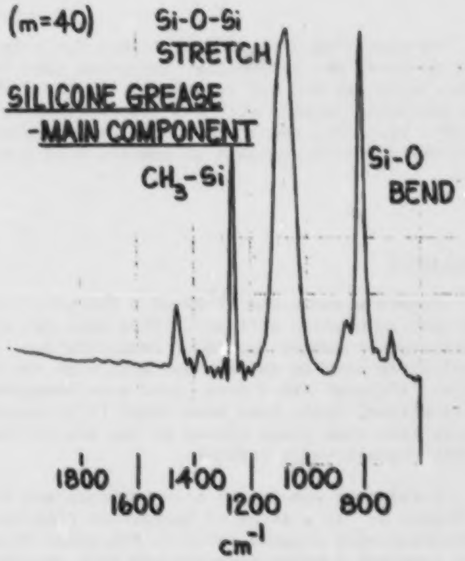

FIGURE 2. FLUIDIZED BED COAL COMBUSTION
MERC/SAMPLE 49, FRACTION #1

Since IR analysis of Fraction 1 has never provided any useful data, it is recommended that qualitative analysis of this fraction should be restricted to low resolution mass spectrometry (LRMS), which may give useful details pertaining to the molecular weight range of hydrocarbons present.

Fraction 2

As in the case of Fraction 1, little useful information is typically obtained by IR analysis of this fraction, and again, LRMS would be a better choice since polycyclic aromatic compounds present give characteristic molecular ions by this technique. Figure 3 shows a typical IR spectrum of a Fraction 2 obtained by Fourier transform infrared (FT-IR) analysis.

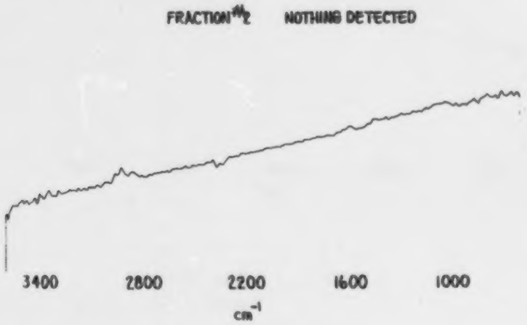

FIGURE 3. EXXON 1601-2
(Level-1 IR, m=10)

On observing data such as Figure 3, it is easy to reach the subjective conclusion that the sample size was too small; however, provided that the analytical sensitivity was that defined by the Level-1 protocol, the correct conclusion would be that the fraction contains no compounds of concern.

Fraction 3

Figure 4 shows the FT-IR of a Fraction 3 from FBC coal combustion effluent. This spectrum reveals another common source of contamination, XAD-2 resin used in the sorbent module of the SASS train. Although XAD-2 does cause some background difficulties, these have been found to be appreciably less than those caused by the use of Tenax as the organic vapor sorbent.

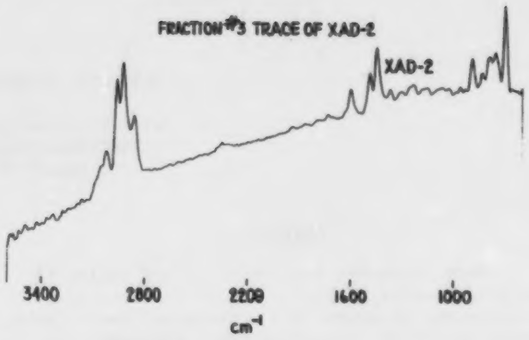

FIGURE 4. EXXON 1601-3
(Level-1, IR, m=10)

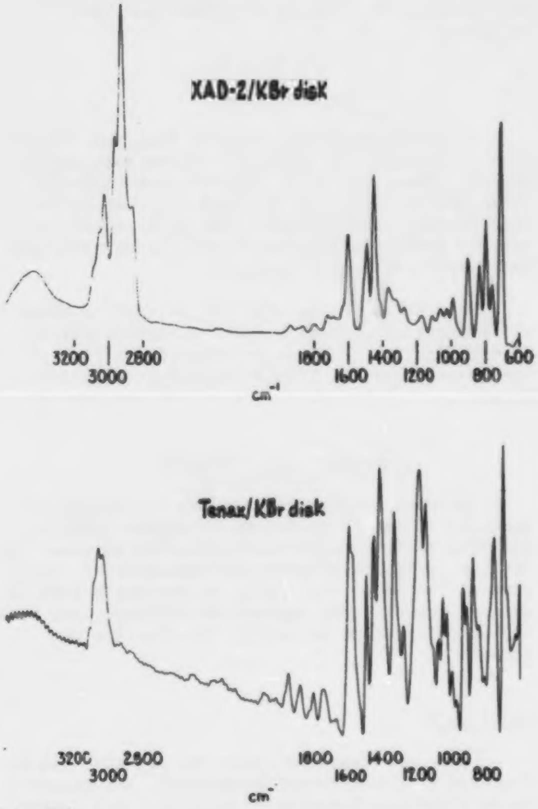

FIGURE 5. IR SPECTRA OF XAD-2 AND TENAX

Referenced spectra of both sorbents are shown in Figure 5. In a study of background problems associated with organic Level-1, Fractions 3 and 4 most commonly exhibit interference from the sorbent used. Figure 6 shows representative IR spectra of contamination originating from XAD-2 and Tenax. Contamination due to the use of XAD-2 is typically not due to the presence of the resin itself, but appears to be either decomposition products or other organic species which may be released from the body of the resin beads. On the other hand, contamination caused by Tenax is most typically solubilization of the resin itself, and as can be seen from Figure 6, is typically about an order of magnitude more severe than with XAD-2. The continued use of XAD-2 in preference to Tenax in this application is recommended, although a lower background would be preferable.

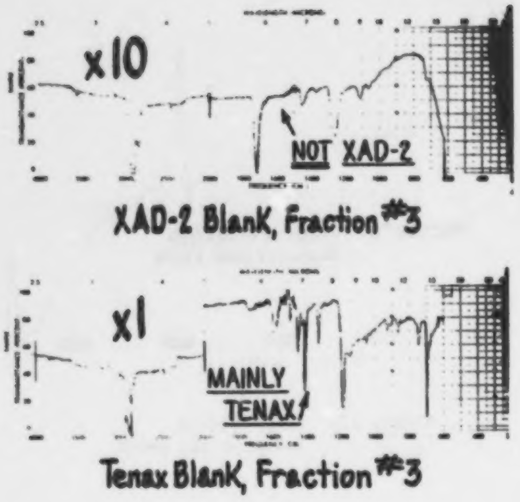

FIGURE 6. IR SPECTRA OF SORBENT BLANKS

Fraction 4

Figure 7 exhibits the presence of a phthalate, which may or may not have been present as an impurity. The concern regarding contamination originating from solvents used is very real, if it is remembered that evaporation of 1 litre of solvent to 10 µl would concentrate a relatively involatile solvent contaminant by 10^5.

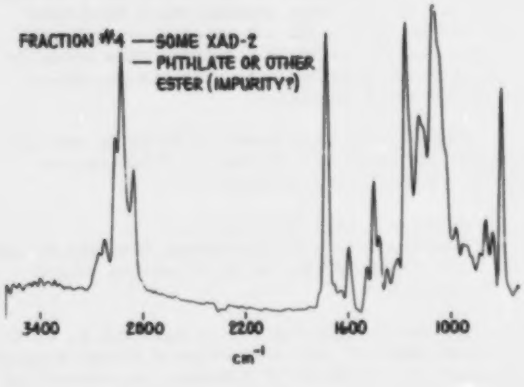

FIGURE 7. EXXON 1601-4
(Level-1 IR, m=10)

In one Fraction 4, shown in Figure 8, IR analysis revealed the presence of large quantities of two different phthalates. We suspect that both may be real in this particular case.

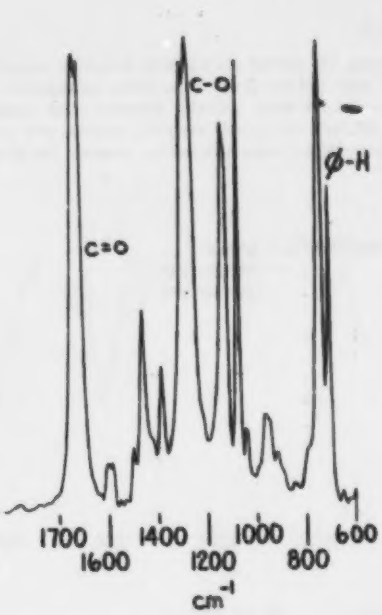

FIGURE 8. YORK RESEARCH-QUENCH TOWER EFFLUENT
(Sample 13a, Fraction 4)

Fraction 5

Figure 9 shows the FT-IR analysis of a Fraction 5 from FBC coal combustion effluent, exhibiting the presence of an ester together with a trace of phenol or amine. In this instance, the weight of Fraction 5 was too small to warrant Level-2 analysis, and thus, the application of the Level-1 protocol obviated the requirement for more extensive analysis.

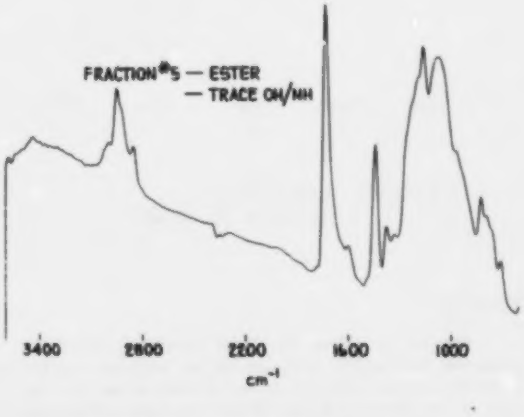

FIGURE 9. EXXON 1601-5
(Level-1 IR, m=25)

Fraction 6

Figure 10 shows extremely intense spectra of an ester and phthalates. In this instance, the phthalates were most likely substituted compounds present in the original sample, since the common plasticier phthalates normally appear in Fraction 4.

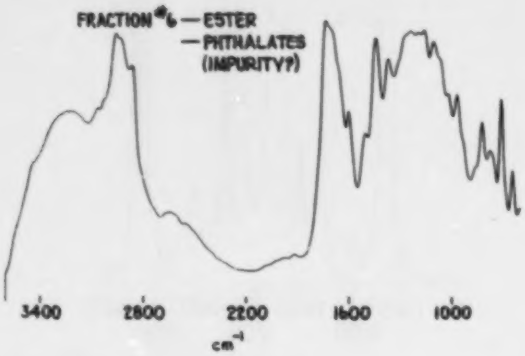

FIGURE 10. EXXON 1601-6
(Level-1 IR, m=100)

Fraction 7

Figure 11 shows a typical Fraction 7 spectrum, containing highly polar species which are probably polyfunctional.

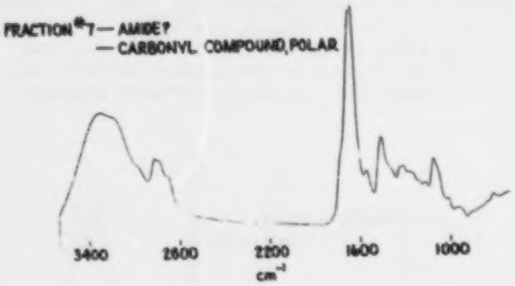

FIGURE 11. EXXON 1601-7
(Level-1 IR, m=100)

Fraction 8

Figure 12 shows an FT-IR spectrum which is rendered virtually useless by an earlier modification to Level-1 in which water was added to the eluate for Fraction 8. This spectrum shows water of hydration, salts, and evidence of solubilization of the silica gel column; the broad water band would mask much available information in the spectrum

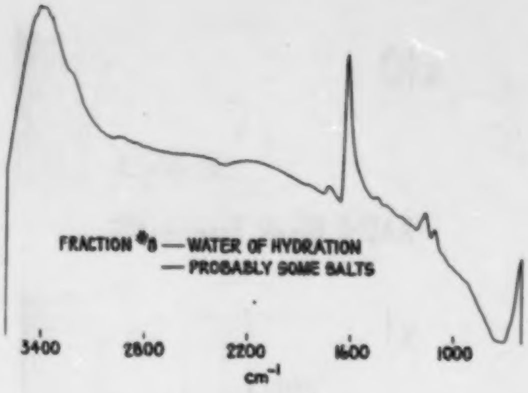

FIGURE 12. EXXON 1601-8
(Level-1 IR, m=50)

While an expected update of Level-1 protocol is expected to delete the analysis of Fraction 8, this may simply be avoiding artificial problems created by the addition of an aqueous eluate to the original non-aqueous LC fractionation scheme. Examining the utility of non-aqueous Fraction 8 eluate may be worthwhile, there does not appear to be any data available in this regard at present. We would agree, however, that Fraction 8 as presently used is of doubtful value.

Note on Use of FT-IR

Although the organic Level-1 protocol requires the use of a spectrometer equivalent to a Perkin-Elmer 521 or 621, many samples which have been analyzed to date could not readily be evaluated without the use of FT-IR. Samples have normally been run successfully, only with the equivalent of 10-20X scale expansion.

However, the real power of FT-IR is that of spectral subtraction. By way of illustration, consider the spectra in Figure 13.

Spectrum A is a Fraction 5,
Spectrum C is a corresponding Fraction 4, and
Spectrum B is the result of subtracting C from A

From preliminary examination of Spectrum A, it is not clear whether this represents a single aromatic compound, or a mixture of several. Spectrum C is readily identifiable as a ketone. Subtraction of C from A yields a spectrum which is readily identifiable as a quinone, which leads to the conclusion that A was in fact a mixture of a quinone and a ketone. Spectra do not always subtract as cleanly as this, but the facile elimination of the blank spectrum from every fraction is a very powerful aid towards interpretation, and highlights the utility of FT-IR.

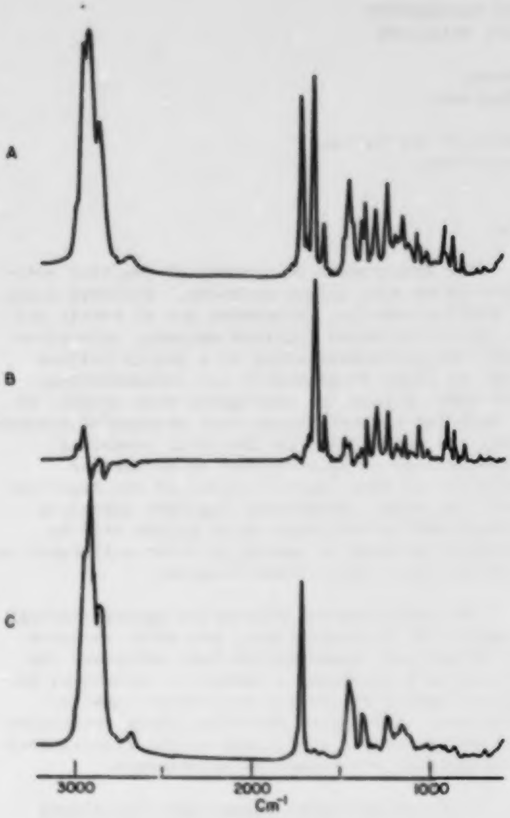

FIGURE 13. EXAMPLE OF THE UTILITY OF SPECTRAL SUBTRACTION BY FT-IR

Note on Use of LRMS

Our experience with LRMS has been that it does not always prove useful, but that when it does do so, the information provided can be very useful. We recommend the continued selective use of LRMS in organic Level-1. LRMS is especially useful for Fractions 1 and 2, it would be useful to delete IR analysis in favor of LRMS for these fractions.

Figures 14 and 15 show ion chromatograms from LRMS analyses where no useful data and a specific compound identification were respectively obtained. Many ion chromatograms which we have observed are similar to Figure 14, which may be due to lack of adequate sample, or volatile compounds which are lost before analysis can be affected. However, strong ion chromatograms such as Figure 15 are observed on sufficient numbers of occasions to merit the use of LRMS whenever the Level-1 fraction weight threshold is exceeded.

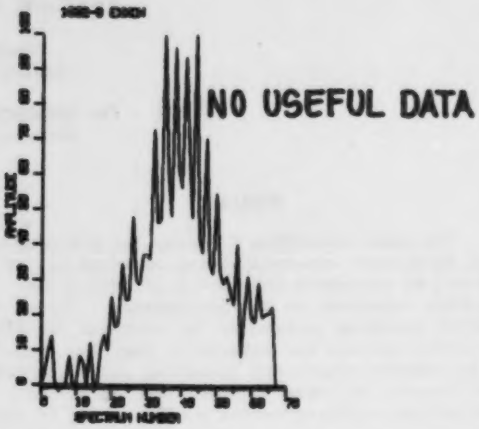

FIGURE 14. EXXON 1602, FRACTION 8

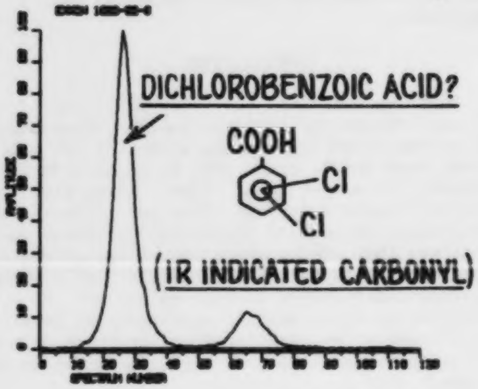

FIGURE 15. EXXON 1023-22, FRACTION 6

CONCLUSION

In conclusion, we wish to reiterate some of the more important points raised earlier:

- Avoid use of silicone grease,
- Use highest purity solvents, recognize that some phthalates may be "real",
- Use of a non-aqueous Fraction 8,
- Utility of FT-IR for spectral subtraction,
- Discontinue IR analysis in Fractions 1 and 2 in favor of LRMS.

Finally, we would reiterate that it would, indeed, be surprising if changes to the Level-1 organic protocol did not continue to be made. Whenever improvements in the analytical strategy become evident, it is important that these should be communicated to the analytical community as soon as possible.

ENVIRONMENTAL ASSESSMENT MEASUREMENT TECHNIQUES FOR FUGITIVE EMISSIONS

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Abstract

The paper describes the sampling and measurement techniques currently being employed or developed to determine the impact of industrial fugitive emissions on the environment. Three general sampling techniques for airborne fugitive emissions and one for waterborne fugitive emissions as stormwater runoff are presented and evaluated with respect to their inherent accuracies and limitations. Site-specific modifications of the general techniques used in recent studies at a variety of industrial locations are described and the results of the measurement programs reviewed. Efforts toward the development of a fugitive ambient sampling train for the measurement of airborne particulate and organic emissions are summarized.

Introduction

Fugitive emissions are those pollutants that are transmitted into the ambient atmosphere or into ground or surface waters without first passing through some stack, duct, pipe or channel designed to direct or control their flow. Known also as non-point source emissions, they are generated by such a large variety of industrial processes and operations that almost every industrial site must be presumed to include some degree of environmental pollution attributable to such emissions. No environmental assessment at an industrial location can, therefore, be considered complete unless an accounting of the impact of fugitive emissions is included.

It is impossible to generalize as to the impact or magnitude of fugitive emissions at industrial sites. The almost endless variety of combinations of site-specific parameters affecting the generation and transmission of fugitive emissions; such as the number, size and locations of sources; site topography; and local meteorological conditions; requires that each site be considered individually. The relative magnitude or impact of such emissions as compared to that of the more traditional point source emissions can, however, be assumed to be generally increasing. Improvements in programs to control many point source emissions, fostered by both technological advances in control equipment and more rigorous enforcement of emissions regulations, have effectively reduced the impact of such emissions. The remaining uncontrolled fugitive emissions have thus been increased in relative impact, in some instances even to the degree of becoming the prevalent source of pollution at a site.

The measurement of industrial fugitive emissions poses some unique problems. Standard stack or similar sampling techniques are of little use in typical airborne fugitive emission situations where the pollutants exist in a poorly defined plume or cloud in generally low concentrations. Grab samples from the atmosphere will usually be of such low concentrations that meaningful measurements are impossible, or they will contain a preponderance of point-source or background pollution so that identification of the fugitives cannot be made. Waterborne fugitive emissions transported to receiving water bodies will be similarly diluted or masked by other pollutants so as to preclude their identification.

The Environmental Protection Agency, through a number of its contractors, and other research and industrial organizations have addressed the problems and developed a number of techniques to measure both airborne and waterborne fugitive emissions. This paper describes those techniques that are generally applicable to the requirements of industrial environmental assessments.

Fugitive Emissions Measurement Techniques

Airborne Emissions

Airborne industrial fugitive emissions may, in general, be measured at their source, before the pollutants begin to diffuse into the ambient air; in the air immediately surrounding their source, where the diffusion is limited to a relatively small volume of air; or in the ambient, where the diffusion is extensive. The measurement techniques currently in use or under development are, respectively, the quasi-stack, roof monitor and upwind-downwind sampling methods.

The techniques, described below, may all be used with suitable samplers and analysis procedures to measure both particulate matter and gaseous pollutants. Modifications or adaptations to the equipment or procedures may be required to meet special needs for sampling a few specific pollutants, but the techniques as described may be generally considered to be applicable to all classes of airborne pollutants.

Quasi-stack Sampling(1)

This method captures fugitive emissions at their source in a temporarily installed hood and transmits them through a duct of regular cross-sectional area where standard stack sampling techniques are used to measure the pollutant concentrations and the flow rate of the emission-carrying air stream. Pollutant source strengths are then determined as the product of these two measured values. A simplified quasi-stack sampling system is shown in Figure 1.

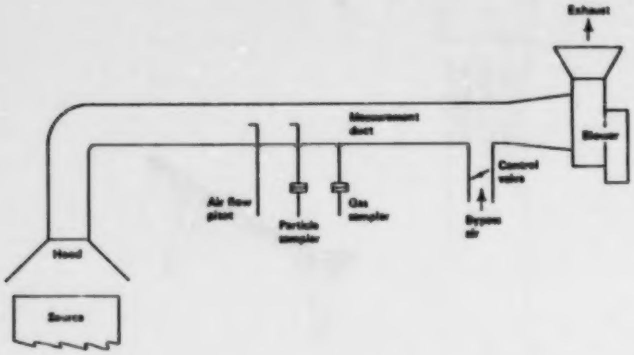

Figure 1. Simplified quasi-stack sampling system.

The quasi-stack sampling method is the most accurate of the fugitive emissions measurement techniques since it captures virtually all of the emissions from a given source and conveys them with a minimum of dilution by transport air to their sampling devices. Accuracies in the range of ±25% can be achieved with a carefully designed system. This method is also the least applicable of the techniques since its use must be restricted to those emission sources that can be physically and operationally isolated and are arranged to permit the installation of the system in a manner that will not interfere with normal plant operations or alter the character of the emissions or their generating process.

Roof Monitor Sampling(2)

This method is used to sample the emissions from processes or operations taking place within buildings or enclosures with only a small number of openings to the ambient atmosphere. The structure serves as a large hood, confining the emissions to a finite volume of air before transmitting them through an opening, such as a roof monitor, wall vent, door or window, to the outside air.

Samples of the emissions are taken at the opening, using hi-vol or similar filter-type samplers for particulate emissions and either grab sampling or portable gas analyzer trains for gaseous emissions, to determine their concentration in the transport air. The transport air flow rate through the opening is also measured, using the standard techniques. The combined source strengths of all sources producing emissions inside the enclosure is then determined as the product of the measured concentration and flow. Figure 2 shows an arrangement for obtaining samples and flow data by traversing a set of instruments across a roof monitor. A number of such arrangements or a network of fixed instruments may be utilized for large area openings.

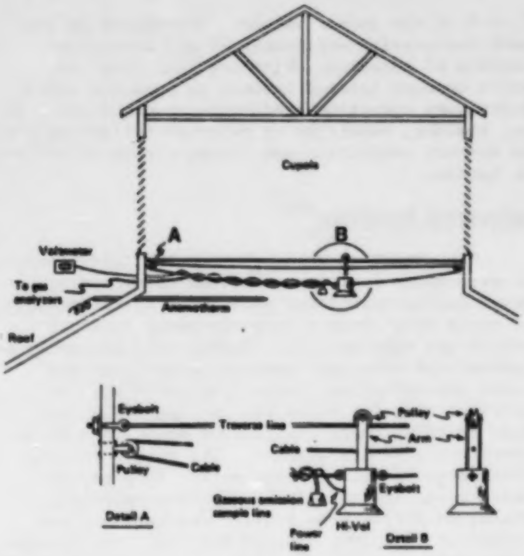

Figure 2. Traversing roof monitor sampling system.

The roof monitor sampling method is not as accurate as the quasi-stack method since a significant portion of the emissions generated within the enclosure may escape measurement through other vents and since a much higher degree of dilution by transport air occurs before sampling. Accuracies in the range of ±50% can be expected with a well designed system. This method is generally more applicable than the quasi-stack method since it does not require the isolation of sources and will not interfere with normal plant operations. It does, however, require instrumentation and trained personnel capable of making measurements of usually low air velocities through relatively large openings and involves mass balances of small quantities of materials.

Upwind-Downwind Sampling(3)

This method may be used to measure the emissions from almost any source after they have been transmitted into the ambient air. Emission concentrations are determined in samples taken from the air approaching (upwind) and leaving (downwind) a source or an entire industrial site, and the source contribution determined as the difference between the measured values. Hi-vol samplers are usually employed for particulate matter and grab samples for gaseous emissions. The calculated source contribution is then used in proven diffusion equations usually embodied in computer programs, along with the measured wind speed and direction and topographic data, to back-calculate the emission source strength.

The upwind-downwind method is the least accurate of the fugitive emissions sampling techniques since only a small portion of the emissions can be sampled for analysis and the flowrate of the large volume of transporting air cannot be directly measured. Measured values of pollutants can generally be expected to be within a factor of

2 or 3 of the actual values. The method is the most universally applicable of all techniques, capable of measuring emissions from large and small sources located indoors or outdoors under almost any operating conditions or schedules. It is, however, sensitive to external influences such as weather conditions and changing wind directions or speeds.

Waterborne Emissions(4)

The principal mechanism for the transportation of waterborne fugitive emissions to receiving water bodies near industrial sites is the runoff of storm water from relatively heavy rainfall events and melting snow. Runoff will typically be encountered from such sources as material and waste storage piles, large open areas such as material transfer yards and parking areas, and flat building roofs that do not drain into storm sewers or drainage systems. The runoff may contain suspended particulate matter from ground-based materials or settled airborne emissions, dissolved solids from similar sources, and suspended or dissolved liquids and oils from process operations, spills, and leaks. Such runoff may be sampled for analysis either as overland runoff as it flows on the ground surface near its source or in open channels where such runoff collects in its flow path to the receiving body. The contribution of pollutants from a specific source or combination of sources is determined by analyzing runoff samples taken at short time intervals to establish the concentration of the pollutants as a function of the simultaneously measured rainfall or runoff flow. Integration of the area under a curve plotted of measured concentration versus total flow or rainfall then provides, by extrapolation, the amount of pollution that can be expected for any rainfall or snow melt. In combination with historical precipitation data, this procedure provides an estimate of seasonal or annual pollution.

Runoff sampling is, in general, most effectively conducted during rainfall events when the rainfall rate is high enough to produce visible runoff within about a half hour of its onset and which continues for several hours thereafter. Samples of overland runoff are obtained in collection plugs similar to that shown in Figure 3. A number of plugs are driven into the ground at locations near the source before the onset of the rain so that their top faces are just below the surface of the surrounding ground material. The runoff then flows across the top screen which restricts the flow of entrained particulate matter and permits suspended particles and dissolved materials to pass into the plug. The plugs are manually collected and replaced at appropriate intervals during the storm event to provide data on the decrease in pollutant concentration from the usually high concentration "first flush" as the total rainfall and runoff flow increases. Rainfall measurements are made at about the same intervals to establish the total flow and flow rate as a function of time.

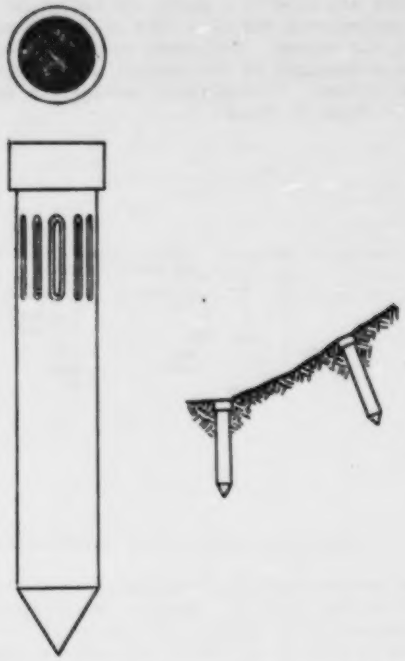

Figure 3. Overland runoff sampling plug.

Open channel runoff is sampled by dipping collection bottles directly into the runoff stream, either manually or with an automatic sampler that can be preprogrammed to collect up to four separate samples in rapid sequence at selected intervals. Runoff flow in the channel is measured using temporarily installed weirs or flumes. All samplings and measurements are made at appropriate intervals to provide data on the concentration - flow - rainfall relationships.

These measurement techniques are generally applicable to all relatively large sources of waterborne fugitive emissions. While their accuracies are difficult to quantify, since no method to accurately determine the absolute levels of pollution attributable to a source exists, it is reasonable to assume that the values obtained will be within a factor of 2 or 3 of the actual values.

Measurement Method Applications

The basic techniques described above for the measurement of fugitive emissions have been used, with modifications to meet the requirements for the sampling of specific pollutants or sources, by a number of organizations in recent years with varying degrees of success. This section reviews a few of the more successful applications of the techniques to illustrate how they might be used in industrial environmental assessments.

Quasi-Stack Measurements at a Gray Iron Foundry(5)

As one phase of an Environmental Protection Agency sponsored contract to develop fugitive emissions measurement techniques, an environmental consultant performed a quasi-stack sampling program to identify and quantify the fugitive emissions generated by the pouring and subsequent cooling of a medium-sized gray iron casting in a sand mold.

A capture hood that enclosed the mold on three sides was fabricated from sheet metal and connected to a horizontal duct of circular cross section. An exhaust fan was utilized at the end of the duct to draw the emissions through the duct to the sampling ports. An Ikor continuous particle monitor was connected at one sampling port to measure dry, filterable particulate matter; an EPA Method 5 Particulate Train was connected to another port to measure particulate matter, organic and inorganic condensibles, particle size, and particle size distribution; and a Cascade Impactor with an EPA Method 5 Condensible Train connected at a third port to provide additional measurements of particulate matter, organic and inorganic condensibles and particle size distribution. These three redundant samplers were used as part of the developmental study to evaluate the sampler effectiveness. In a normal environmental assessment measurement program, only one would be used. A fourth sampling port was used to draw gaseous samples through a flame ionization detector for total hydrocarbon analysis and a non-dispersive infra-red analyzer for carbon monoxide analysis. The test set-up as installed at the foundry is shown in Figure 4.

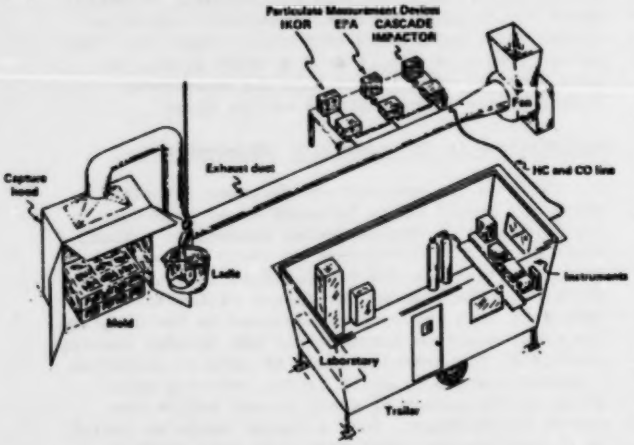

Figure 4. Gray iron foundry quasi-stack sampling arrangement.

The hood opening and fan were designed to provide a face velocity of 150 feet (46 meters) per minute at the opening, ensuring the capture of the exhaust gases from the pouring and cooling operation. The duct diameter was sized to provide an exhaust gas velocity of 2500 to 3000 feet (770 to 925 meters) per minute, sufficient to ensure that particle deposition in the duct due to settling would not occur.

The results of a series of 23 separate pourings of castings ranging in size from 250 to 1000 indicated that the emissions were, in total, not significantly different from the background emissions in the foundry. The continuous particle monitor traces showed an instantaneous peak value of particulate emissions about an order of magnitude higher than the average reflected by the other samplers, but the peak was of such short duration that the total particulate loading was almost unaffected.

Roof Monitor Measurement at a Graphitizing Plant(6)

In a program designed to prove compliance with air pollution regulations, a manufacturer of carbon and graphite products performed a study of its total plant particulate emissions using the roof monitor technique. The plant contains a large variety of process operations, each producing particulate emissions at different rates and on varying schedules, with the total of all process emissions being transmitted to the atmosphere through a large roof monitor. A careful study of the flow patterns at the monitor determined that samples taken at three locations in the monitor would provide data representative of the total roof monitor flow.

The emissions were sampled simultaneously and continuously at the three selected locations using standard hi-vol filters modified to permit directional sampling from below. Air flow rates through the filters were maintained at about 1.3 to 1.4 cubic meters per minute as indicated by rotameter measurements at each location. Filters were changed when the lower flow rate was indicated. This flow range provided sampling at slightly less than the isokinetic velocity and biased the measured values of concentration slightly toward the high side. Actual roof monitor air velocities at each sampling location were monitored with propeller electronic anemometers connected to strip chart recorders to provide a continuous record. Volumetric flow rates were then calculated using integrated averages of the measured velocities.

The results of a week of continuous sampling, with filter changes providing average values for periods of from 1 to 15 hours, showed average particle emission rates for the plant of from 1 to 9.5 pounds per hour. Correlation of the measurements with a log of plant activities enabled the estimation of emission rates for specific processes, which is necessary information for planning a control program if the need for controls is established.

Upwind-Downwind Measurements at Integrated Iron and Steel Plants(7)

As part of an EPA sponsored study to determine fugitive emission factors for a variety of open sources at integrated iron and steel plants, a research organization performed a series of measurements of the particulate emissions generated by slag loading operations using a modified upwind-downwind technique.

This loading operation, which utilizes a high loader to transfer the slag from a storage pile into trucks or rail cars, takes place in an open area and produces an intermittent cloud or a series of puffs of high concentration suspended particulate matter. In order to effectively isolate the emissions from the loading operation, samples had to be taken within the cloud as close to the source as possible. To accomplish this, the contractor designed and fabricated a portable sampling system mounted on a trailer that could be positioned within a few meters of the vehicle being loaded. The sampling system consisted of a tower, 6 meters high, with a 5 meter crossarm located about 4.5 meters high. Exposure sampling heads, containing a settling chamber for large particles and an 8 x 10 inch glass fiber filter, were mounted at heights of about 3 and 6 meters on the tower and about 0.7 meter from the tower centerline on each side of the crossarm. Smaller samplers, containing 2 inch diameter glass fiber filters, were mounted on each side of the cross arm about 2.4 meters from the centerline. A high volume cascade impactor and a standard hi-vol filtration unit were mounted as close to the tower as possible at cross arm height to provide particle size distribution data and back-up exposure data. The arrangement of the sampling heads was designed to encompass about 90% of the mass flux of particulate matter in the cloud with the assumption that the particle distribution was normal.

In operation, the inlets of all sampling heads were pointed into the wind and the sampling velocities were adjusted to match the local wind speed as measured by anemometers mounted near the top of the tower and at the base of the cascade impactor. Nominal sampling rates of about 15 cubic feet (0.42 cubic meters) per minute for the four main sampling heads and about 0.75 cubic feet (0.02 cubic meters) per minute for the two auxiliary samplers were varied as required to provide nearly isokinetic sampling.

A series of three samplings was made for loading operations of each of two different slag types containing high (7.3%) and low (3.0%) silt concentrations. Each test sampled, in a 30 to 40 minute period, the loading of from 140 to 175 tons of slag by a 10 cubic yard front end loader. The samplers were run only during actual loading operations. Background particulate concentrations were measured upwind of the source with standard hi-vol filtration units.

The filters were collected and analyzed after each sampling and their exposures plotted versus sampler location. The resulting curves were then graphically integrated to determine the total exposure or mass flux. An emission factor was then determined by dividing the exposure by the mass of the material loaded. This factor was then adjusted by the application of correction factors determined from the measurements to include only particles less than 30 micrometers in diameter and to correct the measured or calculated values to isokinetic conditions.

The emission factors thus determined were in almost perfect agreement in two of the three samplings for each slag type and were consistent with expected influences of silt content. Particle size distributions and concentrations determined with the sampling system were in good agreement with those determined with the hi-vol sampler and the cascade impactor.

Stormwater Runoff Measurements from Utility Plant Coal Piles(4)

As part of an EPA sponsored study to evaluate the nature and extent of non-point source water pollution from industrial operations, a contractor performed a program to measure the stormwater runoff from coal storage piles at electric generating stations located on rivers and the effect of the runoff on the rivers. The program utilized sampling plugs to obtain overland runoff samples at selected locations between the coal piles and the rivers and dip-sampling bottles to obtain open-channel samples in a water discharge canal and at the outlets of covered drains. Flow rates were determined from rainfall data for the overland runoff and from velocity measurements in the channels. Samples of river water were taken at different depths at sampling stations upstream and downstream of the plants and the river flow rates estimated from velocity measurements at a point where the river's depth profile was determined.

The runoff and river water samples were analyzed to determine the concentrations of total suspended and dissolved solids, iron, aluminum, manganese, sulfate ion, and total alkalinity or acidity. The concentrations in the runoff were generally of the magnitudes anticipated and displayed the expected high "first flush" effect, then declined as the rainfall increased to dilute them. The measured concentrations and measured or estimated runoff flows provided reasonable estimates of the total pollutants that would enter the river as the result of runoff from a storm event, but were generally too low to have any measurable effect on the concentrations in the river.

Applications to Environmental Assessments

None of the measurement programs described above was specifically intended to provide data applicable to an environmental assessment. Each, however, in the fulfillment of their various overall objectives did produce data that would be useful in establishing the impact of fugitive emissions from the sources measured in the programs. The quasi-stack measurements of the foundry casting operation, for example, could be used to calculate a representative emission factor relating emissions to the amount of metal poured and/or the number of pourings. Such a factor would be useful in estimating the total emissions that would be generated in any given period based on production schedules.

The roof monitor measurements made at the graphite plant would be directly applicable to an environmental assessment study, either by utilizing the measurements as representative of the total plant emissions or by using the measurements to develop emission factors for the individual plant operations and applying the emission factors to production schedules.

At the integrated iron and steel plant, the upwind-downwind measurements resulting in the establishment of emission factors for a single loading operation could be used to predict the amount of suspended particulate matter from all such operations within the plant. The emission factor data obtained could be used with diffusion equations to predict how much of the suspended particulate matter would be carried beyond the plant boundaries under a variety of meteorological conditions.

The measurements made of the stormwater runoff from the utility plant coal piles could be used to establish factors to relate pollutant generation rates to rainfall intensity, duration and frequency. Used in combination with historical data on past rainfalls, they can predict, with a reasonable degree of accuracy, the pollutant levels that can be expected for any period. The measured values can also be used as input data for modeling the impact of runoff on receiving bodies in programs currently under development.

Measurement Method Developments

The measurement methods and applied modifications described thus far provide the means to measure fugitive emissions from almost any industrial source for environmental assessment purposes. In many instances, however, these methods provide more information than is actually required or are not practical from the standpoints of time or equipment requirements or excessive costs. There is a need for simpler, less expensive measurement methods that may be generally applied to a large variety of fugitive emission sources to provide quicker, if somewhat less accurate results.

The EPA, has sponsored, through its contractors, the development of one such method, the Source Assessment Sampling System (SASS); and is currently sponsoring the development of a second method, the fugitive ambient sampling train (FAST).

The SASS, though not developed for fugitive emissions sampling, has some practical application in the assessment of some sources of fugitive emissions.(8) The SASS is designed to collect particulate matter, organic species and volatile trace elements from point sources. It consists of a stainless steel probe that captures the emissions and transfers them into a convection oven containing three cyclones and a filter assembly that collects and separates particulate matter into four size classifications. The particle-free sample is then passed through a canister of XAD-2 adsorbent resin which removes most of the organics, and into a series of impingers that collect the condensed volatile inorganics. The sample is drawn through the train by a 10 cubic feet (0.28 cubic meter) per minute vacuum pump. A control module provides variable pressure, temperature, power and flow conditions as required for each sampling situations. The SASS is commercially available and is readily adaptable to use any combination of its components.

The SASS has been recommended for fugitive emissions sampling where quick results are desired from sources that enable the estimation or simultaneous measurement of the fugitive emission carrying air stream volume or flow rate. Such conditions exist in many roof monitor type locations and even in a few open plume arrangements. In such situations, the SASS can provide good estimates of particulate matter and organic species emissions with almost no set-up time.

The FAST, designed to provide large samples of particulate matter separated into two size classifications simultaneously with a smaller sample of organics, is currently in the preliminary design phase. The system will consist of two separate portable modules. One module will contain the sampling train consisting of a 200 cubic feet (5.6 cubic meters) per minute cyclone and glass fiber filter for particle collection and a 5 cubic feet (0.14 cubic meters) per minute XAD-2 resin canister for organics. The second module will contain the blower and vacuum pump for the sampling train. The FAST will provide a 500 milligram sample of particulate matter in an 8 hour sampling period at most industrial locations where sampling of pollutants after they have reached the ambient atmosphere is required. The successful development of the FAST will provide larger samples in shorter time periods than is possible with any standard hi-vol sampler now in use, and will greatly simplify and shorten upwind-downwind measurement programs.

Additional developmental effort is required for both generally applicable measurement methods and methods to identify and quantify specific pollutants. An advance in the state of the art to the level now existing for point sources will facilitate the inclusion of fugitive emissions measurements in future environmental assessments, ensuring that the total impact of the emissions from industrial sites is considered.

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SAMPLING AND ANALYSIS PROCEDURES
FOR SCREENING INDUSTRIAL EFFLUENTS
FOR PRIORITY POLLUTANTS

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Abstract

The Environmental Protection Agency agreed to review and revise regulations based on the Best Available Technology Economically Achievable for effluents in 21 industrial categories, as a settlement of several cases in the District Court for the District of Columbia. An integral part of this process is a technical study to determine whether or not compounds from a list of 65 materials (single compounds and undefined classes of compounds) exist in industrial waste waters. The Effluent Guidelines Division in EPA has established an unambiguous list of 129 compounds, referred to as priority pollutants, which it believes fulfills the requirements of the court order and can be determined analytically. To maintain consistent sampling and analytical procedures for 21 industrial studies, EPA has developed a protocol of the sampling and analytical methods to be used for the screening of priority pollutants in waste water. This protocol represents the incorporation of the current state-of-the-art procedures for the sampling and analysis of the priority pollutants. These analytical procedures include: purge and trap gas chromatography-mass spectrometry (GC/MS) for volatile organic compounds; semi-volatile organics are done by a liquid-liquid extraction with GC/MS and metals are determined using an inductively coupled argon plasma emission spectrometer.

The Effluent Guidelines Division within the Environmental Protection Agency (EPA) is responsible for the preparation of industrial effluent limitations guidelines. Part of the development of these regulations, under the Federal Water Pollution Control Act, involves a technical study including treatment technology and waste water analysis. In June 1976, EPA agreed to review and revise regulations based on Best Available Technology Economically Achievable (BAT) for effluents in 21 industrial categories, as a settlement of several cases in the District Court for the District of Columbia.

In order to carry out these responsibilities, EPA developed an analytical protocol of sampling and analytical methods to be used in the screening of priority pollutants in industrial waste waters. The Effluent Guidelines Division, in order to maintain consistent sampling and analytical procedures, minimize duplication of effort and enhance comparability of data for 21 industrial projects, needed this protocol to serve as a reference for the various labs involved. The protocol is specifically titled, *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants.* The protocol, revised in April 1977, represents the incorporation of current state-of-the-art procedures in analytical chemistry. These analytical procedures include: for volatile organic compounds, a purge and trap gas chromatography-mass spectrometry (GC/MS) procedure; semi-volatile organic compounds are determined by a liquid-liquid extraction and GC/MS and metals analysis by atomic absorption or inductively coupled argon plasma emission spectrometry. However, metals analysis is only referenced in the protocol. In as much as possible, the protocol recommends preparation of samples, special apparatus, materials and data reporting formats. Most of all, it should be kept in mind that the protocol does not represent formally approved standard methods at this point in time. The protocol shall be revised in the future, pending the completion of contracts attempting to validate these procedures. Moreover, these analytical methods were developed for use in analyzing all 114 organic compounds in all 21 industries. This means that the protocol has limited applications and in some cases, a more specific procedure may be more accurate.

Before these GC/MS methods were finally selected, several others, such as specific methods by groups of substances, were considered. Various priorities dictated the selection process. One of these requirements was the short time period allowed for each industry's technical study. In order to meet court deadlines, each project had one year in which to survey, sample, analyze and categorize the waste water and treatment systems involved. Not only was time a commodity in short supply, so were the funds.

While analysis by groups may have certain advantages, such as the use of additional, specific GC columns, this procedure takes longer and costs more. The rationalization for the use of more general procedures, was that the protocol is designed for the initial screening phase of a technical study. The technical studies were divided into a screening phase, verification phase and standard setting. For the screening phase, the main focus is to determine the presence or absence and order of magnitude of the 129 priority pollutants. Therefore, GC/MS was selected for screening because it was fast, less expensive than single compounds analysis, and reliable for semi-quantitative work.

Court Settlement Agreement

With the signing of the Settlement Agreement, a broad new program was initiated to control the discharge of dangerous substances into U.S. waterways. The strategy, as articulated in the Settlement Agreement, will focus on regulating discharges on an industry-by-industry basis. Appendix B of the court order listed those point source categories to be studied. They are: Timber Products, Steam Electric Power Plants, Leather Tanning and Finishing, Iron and Steel Manufacturing, Petroleum Refining, Soap and Detergent Manufacturing, Autos and Other Laundries, Plastic and Synthetic Materials Manufacturing, Pulp and Paper Mills, Rubber Processing, Miscellaneous Chemicals, Machinery and Mechanical Products, Electroplating, Ore Mining and Dressing, Coal Mining, Zinorganic Chemicals Manufacturing, Textile Mills, Organic Chemicals Manufacturing, Nonferrous Metals Manufacturing, Paving and Roofing Materials and Paint and Ink Formulation and Printing.

The Settlement Agreement also mandates a schedule for the accomplishment of the program. Industries are to be studied in stages, over a period of years. Technical studies for the several industries in the first group, or stage, were initiated October 13, 1977, with a contractor being required to the maximum extent feasible, to complete their performance within 12 months. Not later than six months after contract completion, a proposed regulation must be published in the Federal Register. Final rules for all 21 industries must be published not later than December 31, 1979.

Appendix A of the Settlement Agreement, lists 65 chemicals and chemical classes generally believed to include the most potentially hazardous substances commonly released into the environment. This list of 65 chemicals and classes of chemicals was refined by EPA into a list of 129 unambiguous specific "priority pollutants" for the purpose of technical studies. The Agency believes that the specific list fulfills both the requirements of the court order and that these compounds, in most cases, can be analytically measured. The protocol then, applies to the organic compounds included in the 129 unambiguous priority pollutant list.

Sampling

The initial characterization (screening) of the varied industrial discharges covered by this program will be made on an analysis of a composite sample. Any scheme for collecting a composite sample is, in effect, a method for mechanically integrating to obtain average characteristics of a discharge. During the screening phase, the sample composite can be used to determine the average characteristics which would be representative of that discharge. Composite samples are those that are made up of a series of aliquots of constant volume, collected at regular time intervals in a single container. The duration of compositing will depend on the type of sample being collected, the type of facility being sampled and the time varying characteristics of the discharge. For the analysis of semi-volatile compounds by liquid-liquid extraction GC/MS, a composite sample is taken using an automatic, peristaltic pump with a timer and a single glass compositing jug. A minimum composite volume of 2-1/2 gallons is required. The sample must be maintained at 4°C during collection, shipment and storage. A teflon-lined cap is used to seal the jug. From this composite sample the following portions are obtained: an acid, base/neutral, and pesticide fraction along with associated blanks plus an aliquot for metals analysis. In addition, a field blank for the automatic sampler is required, using blank water as free from organic interferences as possible, through the sampling system used for each sampling point.

Field sampling for purgeable organics requires special consideration and equipment. The sample container should be a 45-ml screw cap vial fitted with a teflon-faced silicon septum. The sample bottles are filled to overflowing (by grabbing the sample) and sealed teflon side down. Duplicate samples are required along with a blank water sample, because of leakage and because the measurement process is sample destructive. All samples are labeled with waterproof labels.

At each sampling point, additional grab samples are taken for total cyanides and total phenols. In both cases, a new one-liter plastic bottle is used, sealed and maintained at 4°C during transport and storage.

For the purposes of this program, a sample is defined as consisting of: a composite field sample, a composite sampler blank, duplicate grabs for purgeable organics (VOA's), a VOA blank, a cyanide and a phenol grab.

Organics by Purge and Trap - GC/MS

Here again, it should be stressed that the protocol used for the Effluent Guidelines Division was intended only for those organic compounds of the 129 unambiguous priority pollutants, and only for a qualitative and semi-quantitative determination of these compounds during the survey phase of the industrial effluent study.

Of the volatile organic compounds, acrolein and acryloritile are not done by purge and trap. These two substances are determined by direct aqueous injection GC/MS. Direct aqueous injection GC/MS is recommended for all compounds that exceed 1000 ug/l.

In general, the purge and trap method is not suitable for the determination of compounds eluting later than chlorobenzene.

The Tekmar Liquid Sample Concentrator is recommended in this section. Using the equipment settings set forth in the protocol, a sample is injected and purged for 12 minutes and the organics are sorbed on the Tenax-silica gel trap. The sample is heated and desorbed into the gas chromatograph. GC/MS data is collected as soon as the GC/MS vacuum system has stabilized.

Quality control is obtained by the analysis of blank samples. These are carried through the field trips by the sampling contractors and contained in bottles just like the sample is. Precision is determined by dosing blank water with the compounds selected as internal standards—bromochloromethane, 2-bromo-1-chloropropane and 1, 4-chlorobutane and running replicate analyses. A table listing the elution order of volatile priority pollutants is given, along with the characteristic ions.

Organics by Liquid-Liquid Extraction-GC/MS

The method described in this section of the protocol applies to compounds which are solvent extractable. After extraction, a gas chromotographic-mass spectrometric procedure is used except for pesticides. The pesticide fraction is determined initially by electron capture-gas chromatography and qualitatively confirmed by mass spectrometry.

A two-liter sample is taken from the composite sample. The base-neutral extraction is done first at a pH of 11 or greater. Methylene chloride is the extracting solvent. A sample is dried and filtered through sodium sulfate. The next step is to concentrate the solvent by Kuderna-Danish (K-D) evaporation (distillation) fitted with a three-ball macro-snyder (then micro-snyder) column down to a 1.0-ml volumn. The internal standard (10 µl of 2 µg/µl D10-anthracene) is added.

To measure phenols, there is an acid extraction done at pH two or less using the base-neutral extracted water. The same procedure is followed as in the base-neutral fraction.

In any sample where an emulsion forms, thus preventing an 85 percent recovery of solvent, the laboratory should use a continuous liquid-liquid extractor. A description of this procedure may be found in the protocol.

The pesticide fraction is determined using a standard method published in the Federal Register, June 29, 1973. A one-liter sample is used and determined by EC/GC, as previously mentioned. Blank extractions for all of these fractions are also prepared and analyzed.

Each fraction is then separated and eluted into the MS under given chromatographic conditions. Relative retention times (compared to hexachlorobenzene) are listed in the protocol.

A performance criteria is stipulated. In order to begin a run, an operator must demonstrate the ability to chromotograph benzidine at 40 ng for the base-neutral fraction. One hundred ng of pentachlorophenol must be detected before the acid extract run.

For the purposes of our program, three conditions must be met in order to indicate the presence of a compound by GC/MS. First, the characteristic ions for the compounds (given) must be found to maximize in the same spectrum. Second, the time at which the peak occurs must be within a window of ± 1 minute for the retention time of this compound. Finally, the ratios of the three-peak heights must agree with the relative intensities given in tables in the protocol, within ± 20 percent.

Quantification of compounds identified, is done by the internal standard method using deuterated anthracene.

Asbestos

One of the substances included in the original list of 65 from the Court Settlement Agreement is asbestos. As it turns out, this is a very strange material to deal with. Several attempts have been made by EPA, with the cooperation of other agencies, among them the United States Geological Survey and the Bureau of Mines, to define the term asbestos. Short of a major research effort, this substance is still a difficult one to define much less analyze in industrial waste waters. It is this Agency's position to recommend, for the purposes of developing effluent guidelines, the use of the *Preliminary Interim Procedure for Fibrous Asbestos*, using Transmission Electron Microscopy, by C. H. Anderson and J. MacArthur Long, U.S. EPA, Environmental Research Laboratory, Athens, Georgia.

General Overview and Status

The protocol, *Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants*, in its present form, has been in use for almost one year and since the draft version, this protocol has been used for over a year and a half. Many analytical contract labs have worked with the protocol for EPA. Moreover, several industries under study have their own laboratories which are also scrutinizing the applicability of this protocol, along with our EPA laboratories. In short, those methods of analysis recommended by this Agency are being tested in actual field situations and passing the tests!

On November 9-10, 1977, a seminar was conducted by EPA on the subject of analytical methods for priority pollutants. Participants at the seminar included the many contractors doing sampling and analysis for the Effluent Guidelines Division, as well as industrial trade representatives and other interested scientists. The purpose of the meeting was to discuss issues of concern and in general, to compare notes on the various experiences of laboratories working with the methods. The overall atmosphere at the seminar was one of refining, or fine-tuning the analytical procedures. Basically, the protocol has been accepted as a reasonable, logical, workable way of uniformly analyzing waste waters from 21 industries for 129 substances.

Many of the major issues discussed at that meeting in Denver, were resolved or acknowledged for the record. One of the topics of discussion concerned the use of internal GC/MS standards provided by EPA. Some very volatile compounds were being lost. Therefore, it was recommended that individual laboratories prepare their own internal standards for vinyl chloride and methylene chloride. Another useful procedure to alleviate the problem of a water build-up in the tenax trap, is to increase the number of times the silica gel is changed.

On the use of liquid-liquid extractions for semi-volatile compounds, emphasis was placed on the need to use continuous extractors when emulsions are formed. Another procedure to aid in breaking emulsions would be to do the filtration through glass wool packs. In general, it should be kept in mind that an 85 percent solvent recovery should be obtained.

In the testing process, a flaw has been found. It now appears that there is a problem in separating benz(a) anthracene + chrysene and anthracene + phenanthrene and benzo(b) fluoranthene + benzo(k) fluoranthene on the recommended GC column. While these substances might be separated on different columns, the columns selected for use are still considered the best when one is limited to three GC columns for all industrial waste water types during the screening phase. GC/UV or liquid chromatography may resolve the problem during the verification phase.

Further study to improve analytical methods is ongoing. Several contracts have been let through EPA, Cincinnati, on the development and application of test procedures for the specific compounds of concern. The Agency's list of priority pollutants have been divided into groups for this research effort. Not only will these contracts aid in the development and refinement of analytical procedures, they will also use actual field samples in order to evaluate their recommended methods. Any changes which develop out of these contracts shall be used in future revisions of the protocol.

At the present time, it is the position of the Effluent Guidelines Division of EPA to endorse this protocol for use in preparing regulations. The tests of time and use appear to be passed. It now remains for these current state-of-the-art methods to become formally accepted in the near future, by publication in the Federal Register.

ALTERNATIVE LEVEL I ANALYSIS METHODS

by

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Abstract

This presentation includes a description of some modifications and additions to the Level I Analysis Scheme that were used to characterize the emissions from coal gasification plants. While some of these modifications go beyond the intent of Level I analyses, the experience gained from their use should be of value to others performing environmental analyses.

Introduction

The word alternative may convey the concept of replacement; i.e. of using Method B instead of A. Such is not the intent of this presentation. Its purpose is to present some recommendations based on our experience with process measurement analyses as they apply to commercial coal gasification facilities. These recommendations deal with the following:

1. Proposed additions to the EPA Level I Scheme for environmental assessment.(1)
2. Proposed corrections of the Level I Scheme.
3. Considerations for more detailed analyses.

The recommendations described here are based on the analytical results that will be discussed in this presentation. These results were obtained primarily from an analytical screening study of selected samples from operating gasification units.(2) Some results were obtained from a Level I pilot study which is still in progress.

Consideration will be given to the extraction procedures for organics, to IR interpretation methods, and to the potential benefits of UV analyses. Additionally, an alternative scheme for organic analyses will be discussed. First consideration will be given to proposing modifications to the Level I procedure.

Proposed Modifications to the Level I Procedure

Before entering into a discussion of the proposed modifications to the Level I procedures, some background information will be presented to acquaint the reader with the problems that led to these proposals.

Background Information

The work on which this presentation is based was done as a part of an EPA sponsored program (EPA Contract No. 68-02-2147) whose overall objective is to provide a comprehensive environmental assessment of Low BTU coal gasification and utilization processes.

Grab samples from several different commercial scale gasifiers and one pilot scale gasifier were obtained for this study. The purpose of this study was to gain insight into the nature of the samples that will be encountered in the assessment program. A second objective was to gain some concept of the differences between various plants and processes. The samples were obtained during inspection trips which were made to develop an environmental test program. The analyses performed were intended to identify, in a very preliminary manner, the classes of compounds present in each sample which may warrant further attention. A significant part of the analyses followed, in principal, the methods defined by the EPA procedures manual for a Level I Environmental Assessment.(1)

The screening study provided a significant amount of information that was useful to the test program(2) and a number of conclusions were drawn from the results. The conclusions related to:

(a) The classes of compounds and concentrations of components found in specific samples,

(b) The effects of feed stock and process operating condition changes upon levels of key components detected in these samples, and

(c) Modifications/additions to procedures which will help insure that a maximum amount of environmental information is obtained from the program.

This presentation shall deal primarily with matters relating to topic (c).

Extraction of Organics

The extraction procedure defined by the procedures manual for a Level I assessment(1) should be expanded to include more polar extracting solvents. The basis for this need is illustrated by the data in Table 1.

TABLE 1. ORGANICS EXTRACTED FROM A GASIFICATION PROCESS LIQUOR

Solvent	g/10ℓ	%
MeCl	28	37
Ether	38	51
Acid-Ether	9	12

$\frac{\text{Sample}}{\text{Extractant}} = 10/1$ (n) no. of extractions = 3

From these results it is evident that less than half of the organics are being extracted by the methylene chloride at a 10:1 sample to solvent volume ratio. One might conclude that this error is within the ±2 to 3 accuracy specification sought by the Level I objectives. However, it must be recognized that the materials extracted by the ether from the acidified sample might be totally different from those extracted from the neutral sample with methylene chloride. These conditions can be recognized by comparing the infrared spectra of the extract-residue as illustrated in Figures 1 and 2.

The top spectrum shown in Figure 1 was obtained from a methylene chloride extraction of quench liquor from one test site (Site A); the middle was obtained from an ether extraction and the bottom from an extraction with ether after the sample had been acidified to pH = 1. In this experiment, the extractions were carried out sequentially on the same sample. The numerous differences in these spectra confirm that the three extracts contain widely different materials. For example, the carbonyl band in the 1700-1740 cm^{-1} region is absent from the first two extracts and the three bands in the 800 cm^{-1} region - indicative of sulfones - are absent from the methylene chloride extract.

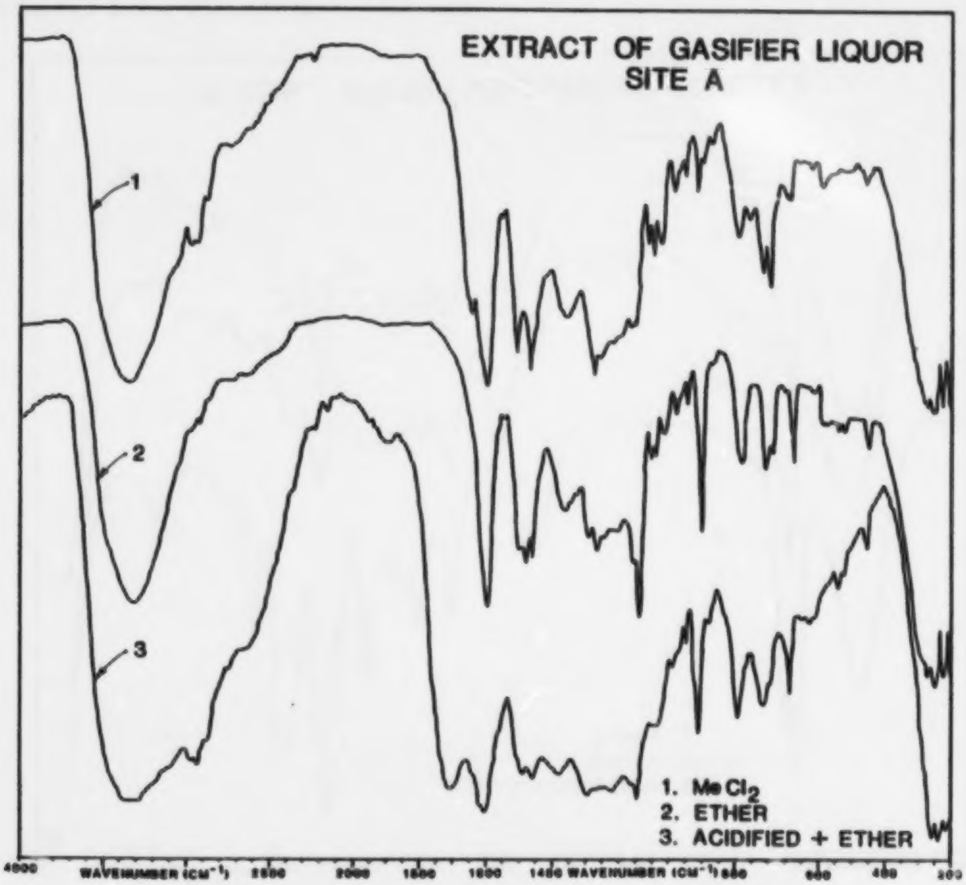

Figure 1. Infrared spectra of three successive extracts of gasifier liquor from Site A. (Sample: Extractant = 1:1, n = 4)

The extracts of a comparable stream from another site were compared. Their spectra are shown in Figure 2. Although the spectra of these extracts were quite different from the Site A extracts, the result was similar; i.e., the ether and acid-ether extracts were indeed different from the methylene chloride extract and different from each other. These differences indicate that methylene chloride does not extract all organic substances from water.

Additional attention should be directed to the sample to solvent ratio. The Level I procedure recommends a 20:1 sample-solvent ratio as a means of concentrating organics into the extracting solvent. This approach is valid only for materials having a distribution coefficient of perhaps five or greater; that is, a substance which has five times the preference for methylene chloride that it has for water. Many polar organics fall outside this limit.

The extractions performed for the screening study were made with a 1:1 sample-solvent ratio and a 4-step extraction. The results are shown in Table 2.

TABLE 2. ORGANICS EXTRACTED FROM SITE A QUENCH LIQUOR (1:1)

Step	mg/ℓ	% of Total Extracted
1 Methylene Chloride	2231	57.7
2 Ether Extractable[a] at pH 7	1457	37.6
3 Ether Extractable[b] at pH 1	177	4.7
TOTAL EXTRACTED	3865	100.0

[a] Following Step 1

[b] Following Steps 1 and 2 n = 4

Equal volumes were used because the sample was rich in organics and only about 500 ml of sample was available. However, it is evident that by using a 1:1 volume ratio, a larger percentage of the organics were extracted by the methylene chloride. Attention is called to the fact that the spectra in Figures 1 and 2 are from extracts that were obtained with a 1:1 volume ratio

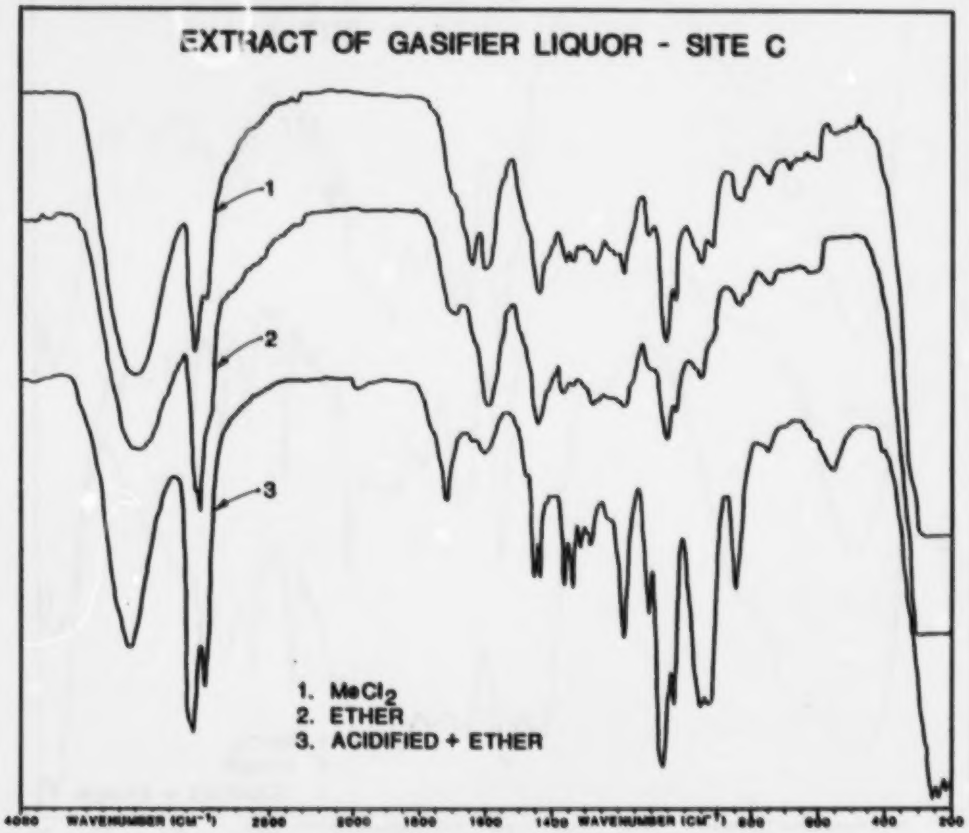

Figure 2. Infrared spectra of three successive extracts of gasifier liquor from Site C. (Sample: Extractant = 1:1, n = 4)

using a 4-step extraction and that these conditions favor a more complete extraction by the methylene chloride. The differences between the methylene chloride extract and the ether extracts could be even greater at the 20 to 1 ratio.

To gain insight into the effect of volume ratios, use can be made of some basic relationships of extraction theory. Equation (1) defines the fraction of solvent transferred (F) in terms of relative extractant volume and distribution coefficient (K_D):

$$F = \frac{K_D V_e}{V_S + K_D V_e} \qquad (1)$$

where: V_e = volume of extractant, and
V_S = volume of sample.

In order to relate the fraction transferred in a single extraction to the total mass transferred by a sequence (E_n) use can be made of the Remainder Theorem defined in Equation (2):

$$E_n = 1 - (1 - F)^n \qquad (2)$$

Figures 3 and 4 depict these relationships graphically. Figure 3 shows the relationship between E_n and F for a 3-step extraction specified by the Level I procedure. Figure 4 shows the relationship between K_D and F at three different volume ratios:

20:1 Specified by the Level I Manual.
10:1 Used in the Pilot Study.
1:1 Used in the Screening Study.

Note that in order to extract 90% of a component in three steps (the point is designated by an arrow in Figure 3), approximately 50% must be extracted per step. In order to achieve a 50% extraction, the solute must have K_D values as follows:

V_S: V_e	K_D
20:1	20
10:1	10
1:1	1

In order to comply with the Level I objective of ±2, the 3-fold extraction must remove 50%, requiring an F of 0.2 and K_D values as follows:

V_S: V_e	K_D
20:1	5
10:1	1
1:1	0.5

In order to be assured that polar species are detected in screening studies and in subsequent analyses, serious consideration should be given to these fundamentals. This work indicates that more favorable volume ratios and a sequence of solvents are needed to characterize the effluents from Low BTU coal gasification processes. However, these principles are applicable to all environmental tests where extractions are used to isolate pollutants.

Infrared

In this section, attention is focused on a problem in the quantitative assessment of infrared spectra for Level I organic analyses. The "Suggested Format for Level I Organic Analyses Data"(3) recommends that spectral intensity be reported relative to the strongest band on a transmittance basis. The practice is undesirable because the results can be highly misleading. The problem is illustrated in Figure 5.

The diagram in Figure 5 shows two hypothetical bands of apparently equal intensity; i.e., they both show 45% transmission relative to their base line. When the transmission is converted to absorbance, the lower band is 3.5 times as strong as the upper band. The reason for this is as follows:

$$0.45 = (0.95 - 0.50) \neq \text{Log}\,\frac{1}{0.5} - \text{Log}\,\frac{1}{0.95} = 2.8$$

$$0.45 = (0.50 - 0.05) \neq \text{Log}\,\frac{1}{0.05} - \text{Log}\,\frac{1}{0.5} = 1.0$$

The fallacy is further illustrated by Figure 6 which shows two spectra of a single sample run at two base line levels. The instrument span was set with no sample in the beam. The sample was inserted and the spectrum run. Then the optical attenuation was adjusted to raise the base line and the spectrum was rerun. In this figure the absorbances (A) and the transmittance ratios of the top and bottom curve are each equal to each other and their ratios are therefore equal to unity, i.e.:

$$\left(\frac{\frac{T}{T_o}\,\text{top}}{\frac{T}{T_o}\,\text{bottom}}\right) = \frac{A\,\text{top}}{A\,\text{bottom}} = 1$$

but:

$$\frac{(T - T_o)\,\text{top}}{(T - T_o)\,\text{bottom}} = 1.7$$

This result illustrates that it is fallacious to use T as a measure of band intensity. To avoid this fallacy, bands must be determined as either absorbances or as intensity ratios relative to the base line.

Clarification is also needed for the measurement of shoulder bands. The practice used for this work was to measure all

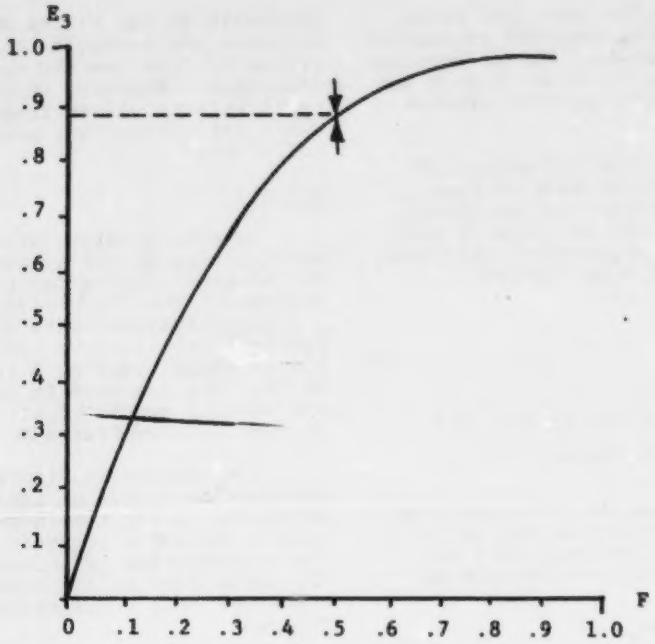

Figure 3. Plot of remainder theorem - relationship between fraction of mass transferred per extraction (F) and total mass transferred on three extractions (E_3).

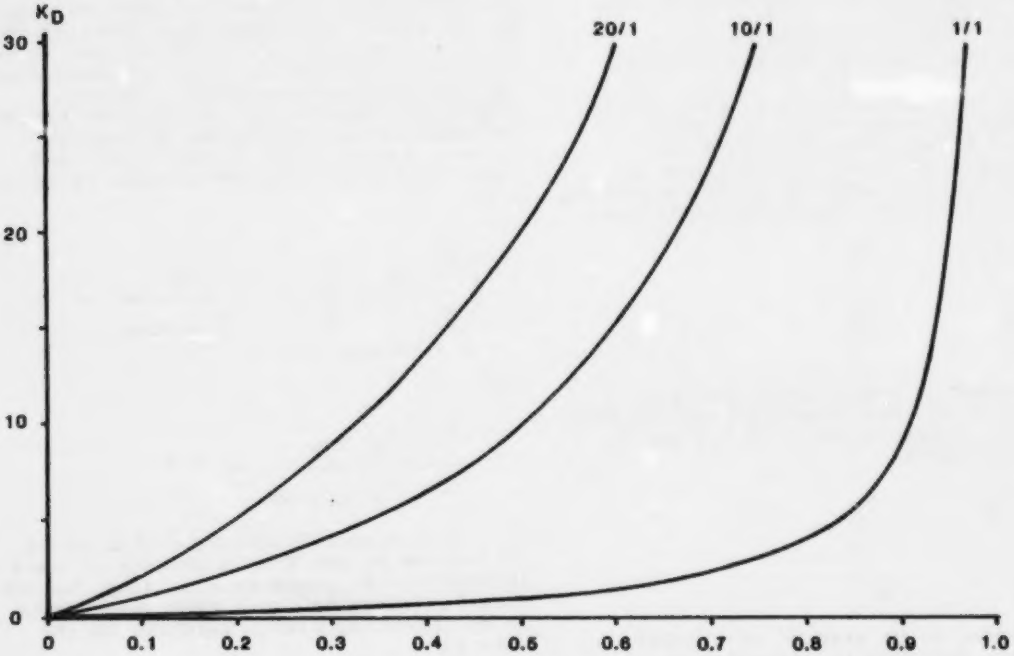

Figure 4. Relationships between fraction of mass transferred (F) and distribution coefficient (K_D) at three different phase ratios.

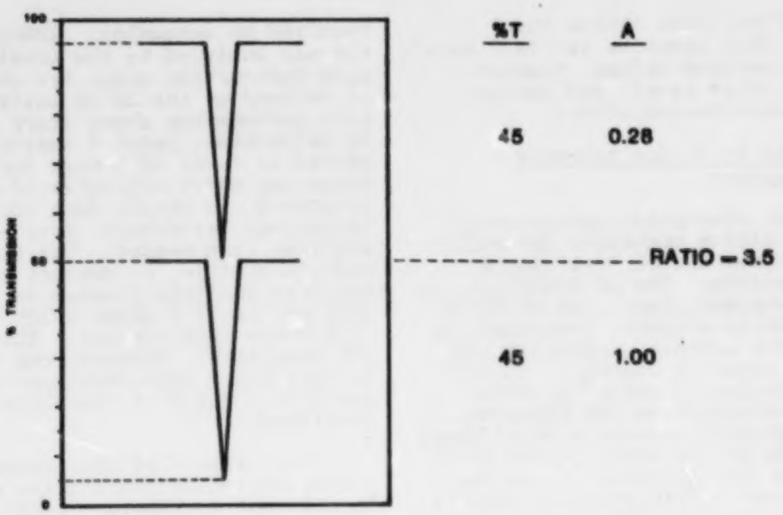

Figure 5. Effect of transmission level on band intensity - Theoretical band of equal transmittance.
Note: 3.5 times as much absorbance is required to produce the band at the lower transmission level.

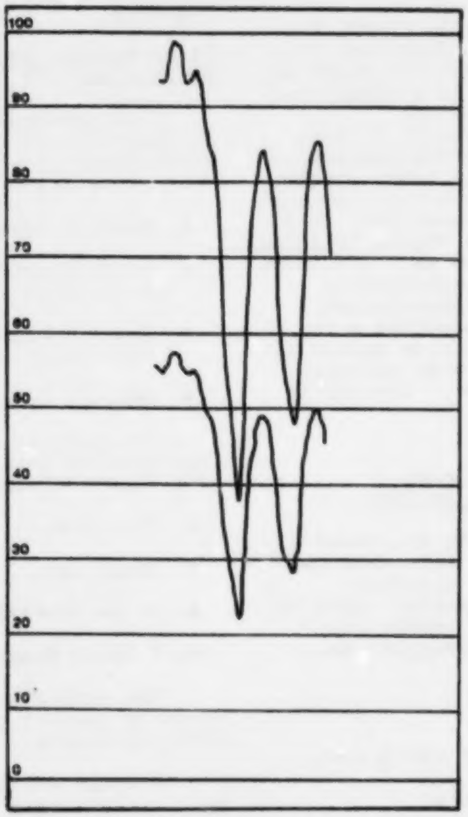

Figure 6. Effect of transmission level on band intensity - Actual spectra of equal absorbance ($A_{top} = A_{bottom}$). Both spectra were obtained with the same sample, only the reference beam energy was attenuated.

bands from the base line rather than tangentially. This practice is "fail safe" since it gives maximum values; however, it may produce false levels and thereby contribute to misdirected effort.

Benefits Offered by UV Spectrometry for Level I Analyses

Ultraviolet absorption spectrometry is a highly sensitive technique for polycyclic hydrocarbons and it is a simple technique to perform. The LC fractions can be scanned in minimal time. The UV absorbance of polycyclic aromatic components is very strong. For example, materials such as anthracene, shown in Figure 7, exhibit molar absorptivities of about 10^5 which enables their detection at the nanogram level. An additional advantage is afforded by the principle of the Bathochromic shift that accompanies the increase in the number of fused rings. This property permits polynuclear components to be detected in the presence of other aromatic compounds. It should be practical therefore to use UV spectrometry to screen samples and LC effluents (particularly the early fractions) for evidence of polycyclics in the presence of other aromatic compounds.

The spectra in Figures 8, 9 and 10 illustrate this potential. Fraction LC-2 of tar in Figure 8 shows distinct peaks at about 320 and 340 nm which is a clear indication of polynuclear substances. Similarly, LC-3 of tar in Figure 9 shows a peak near 330 nm plus a sharp maximum of 250 nm, with a significantly lower absorbance at 220 nm. This is clear evidence of polynuclear aromatics. In contrast, LC-5 from gasifier condensate in Figure 10 shows minimal absorbance above 300 nm. The curve shape is characteristic of substituted aromatic compounds such as phenols etc. UV spectrometry therefore provides a potentially useful, cost effective method of screening effluents or effluent extracts for polynuclear hydrocarbons. Its use is recommended.

Extensions to the Level I Procedure for Organic Analysis

Many streams examined by the Level I procedure during this study were observed to contain large amounts of organics. However, the presence of organics could be established by various means other than the Level I analyses. For example, use could be made of:

- Process Flow Sheets,
- Engineering Analysis of the Process,
- Visual Observation, and/or
- Olfactory Sampling (Smelling).

Samples such as tar were, by their very nature, polyaromatic and therefore required no screening. (During the study, tar was analyzed by the Level I method to gain information about its characteristics as defined by the LC-IR analysis and to gain information about trace elements.) By definition, Level I analyses could be waived in favor of a more detailed analyses. Since one major objective of the Low BTU program is to obtain data for a control technology assessment, more specific type-analyses were needed. The decision was made, therefore, to conduct a species-specific analysis-program in conjunction with the Level I pilot study, using essentially the same samples. This work is not yet completed. However, the methods used in this study were developed and tested previously and will therefore be described.(5-7)

The essence of this method is a preseparation-derivatization scheme that is designed to separate materials into classes and make them compatible with the GC Mass Spectrometer. This approach is well founded, in view of the resolving power of the GC-MS and the searching power of the data banks. However, even without the support of the GC-MS, the LC separation scheme is a useful tool for characterizing organics.

Preseparation by Liquid-Liquid Extraction(5-7)

The preseparation scheme illustrated in Figure 11 is based on liquid-liquid extraction. It separates the sample into four principal fractions:

- Neutral Lypophylic substances,
- Organic acids whose salts partition into water at high pH,
- Organic bases whose salts partition into water at low pH, and
- Neutral Hydrophylic substances.

The neutral substances are further separated by column chromatography on SiO_2 into four fractions:

- Paraffins,
- Aromatics,
- Polar Neutrals, and
- V Polar Neutrals.

The acid fraction is methylated in two steps to convert phenols to ethers and the acids to esters.

A total of eight fractions is obtained, each containing a distinct class of compounds defined by their solubility and polarity. Each fraction is easily separated by gas chromatography since optimal columns can be selected for each type of material. Tailing is minimized. Similarly,

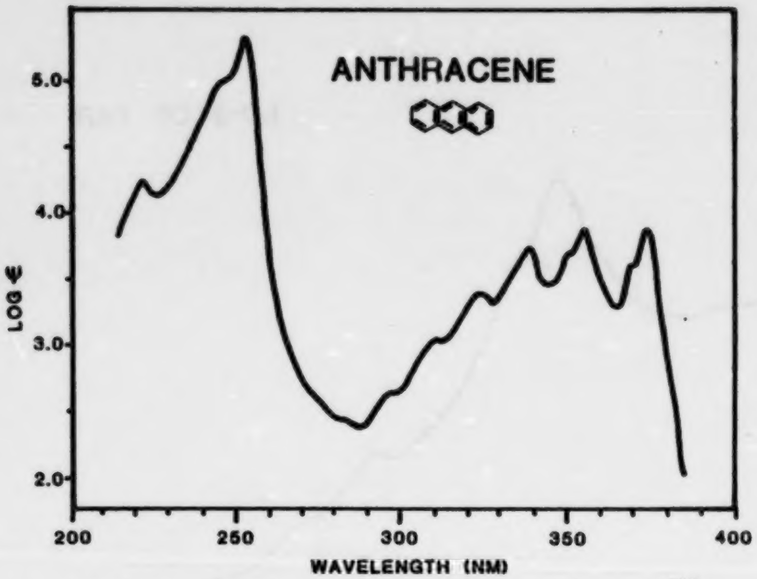

Figure 7. Ultraviolet spectrum of anthracene(4).

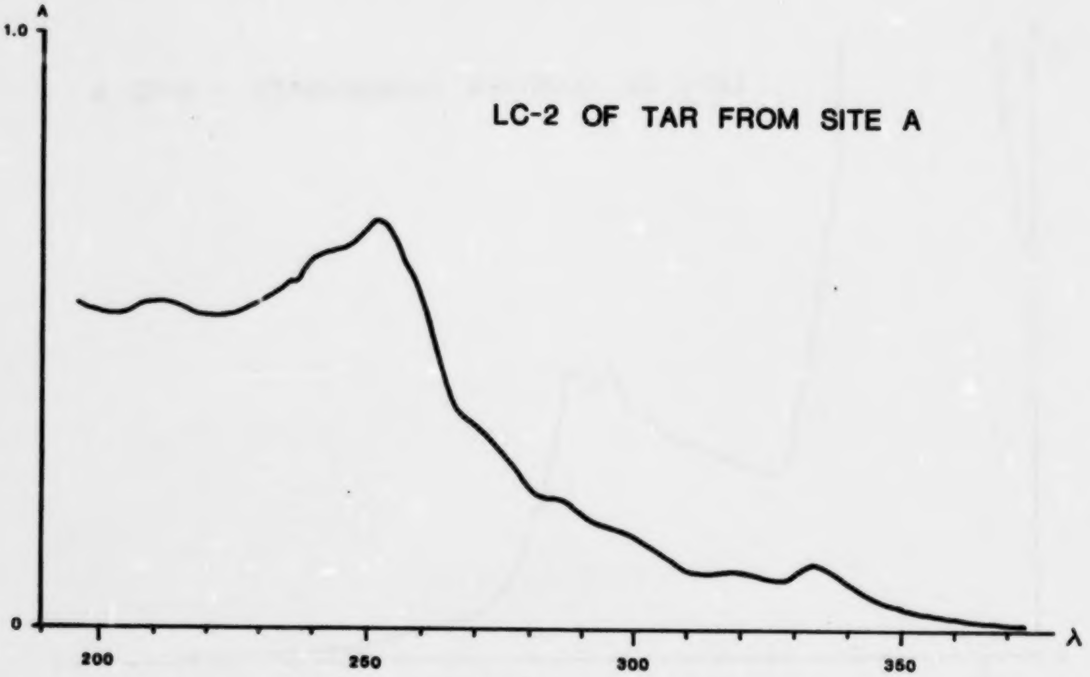

Figure 8. Ultraviolet spectrum of chromatographic fraction 2 from gasifier tar.

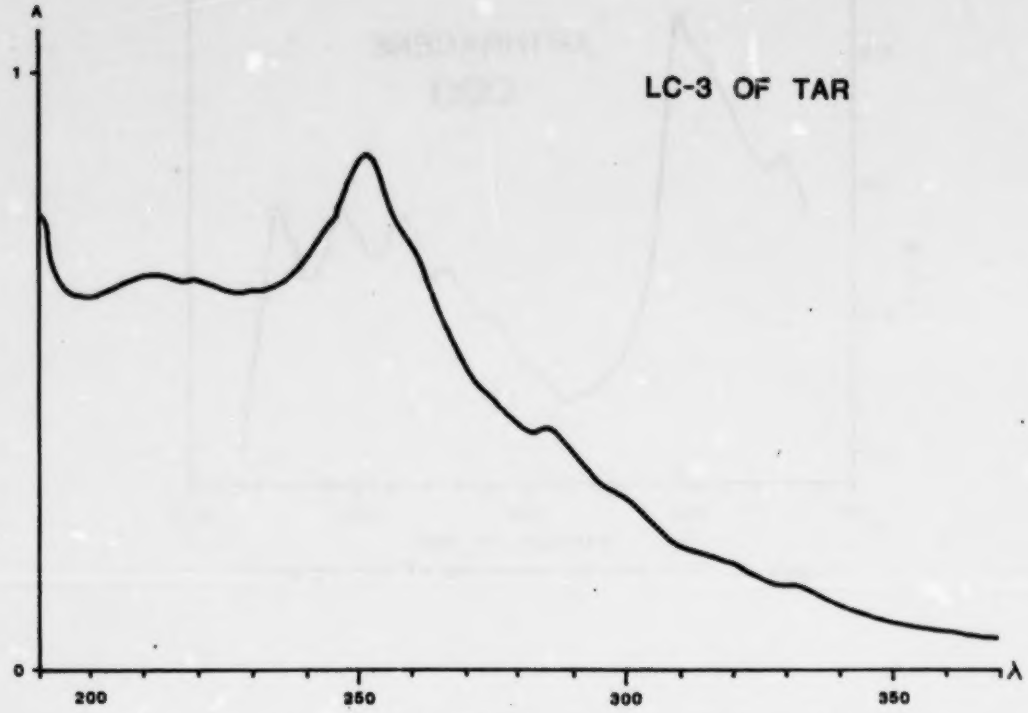

Figure 9. Ultraviolet spectrum of chromatographic fraction 3 from gasifier tar.

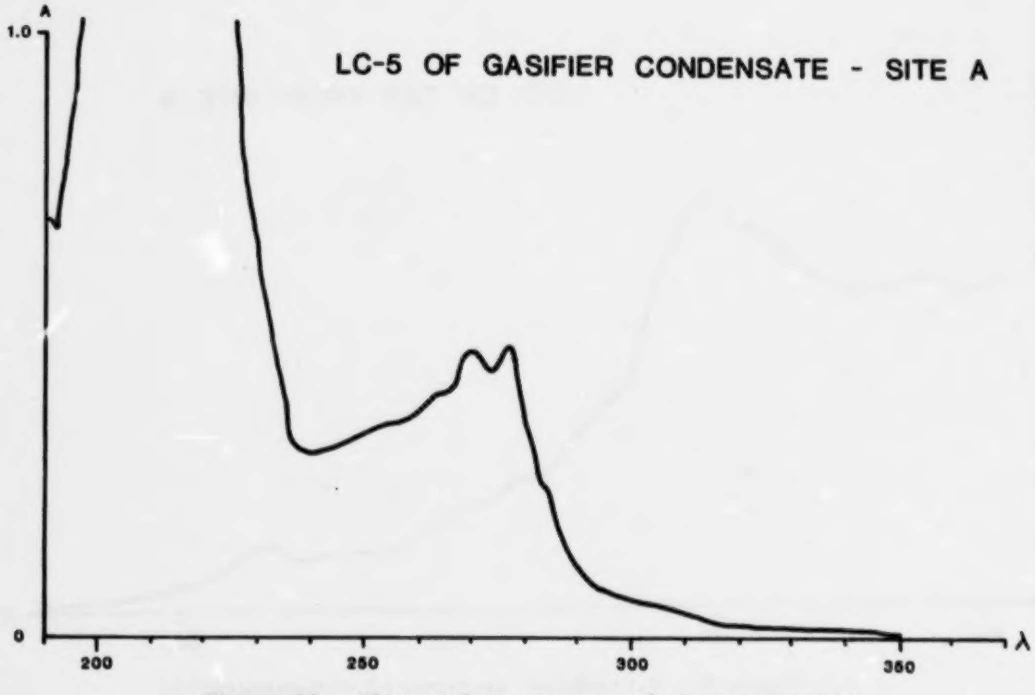

Figure 10. Ultraviolet spectrum of chromatographic fraction 5 of gasifier condensate.

non-volatile substances can be taken as needed for separation by HPLC using an optimal column.

Recovery Studies

This analysis scheme was used to characterize a condensate from a fuel synthesis process.(7) Recovery studies were completed as a part of that investigation. Some typical results are included here.

Figure 11 shows the recovery of aromatics. A 78% recovery was realized. Significantly only 1.5% of the material was found outside of the intended fraction. Figure 12 shows the recovery of acids and phenols which were methylated by dimethyl sulfate followed by methylation with diazomethane. A 78% recovery was also realized with the phenols. Only 3% was found outside of the intended fraction.

The acids were less "selective" as is seen in Figure 13. In this case, 24% were methylated with dimethyl sulfate and the remaining 50% were methylated with diazomethane. Total recovery was 84%. No material was found outside of these fractions.

Methylation of phenols by DMS is by no means stoichiometric. However, yields are reasonable and improvement is believed to be achievable. The data in Table 3 shows some results with known compounds. Early work reported in the literature shows that much higher conversions can be achieved with optimized conditions.

Summary

The ABN separation provides a versatile method for characterizing organics. It can be used for both bulk characterization and detailed analyses by GC-MS and/or other ancillary techniques.

The merit of a liquid-liquid separation cannot be overstated. As a bulk to bulk separation between discrete compounds (e.g., water and solvent) it is highly reproducible. Uncertainties associated with surface properties (adsorption) are eliminated. As a bulk separation, it enables large quantities of sample and of solute to be handled easily. Acids and bases of known concentration can be used to influence the solubility (i.e., the partition coefficients) of the sample, making it possible to handle a wide range of substances with the same system.

The principle disadvantage is that only a single stage of separation is practicable, however, this limitation is readily compensated by the resolving power of the GC-MS.

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TABLE 3. METHYLATION OF PHENOL MIXTURE USING THE DIMETHYL SULFATE PROCEDURE AS DESCRIBED BY WEBB (WE-158)(7)

Compound	Amount Added, mg		Amount Found, mg	% Recovery
Phenol	204		37	18
o-Cresol	257		199	77
m-Cresol	258	479	412	86
p-Cresol	221			
2,6-Xylenol	122		91	75
2,4-Xylenol	102	207	124	60
2,5-Xylenol	105			
3,4-Xylenol	126		103	81
3,5-Xylenol	102		96	94
Hydroquinone	100		47	47
1-Naphthol	106	206	264	129
2-Naphthol	100			
Pyrogallol	100		0	0
TOTAL	2008		1286	Average 64

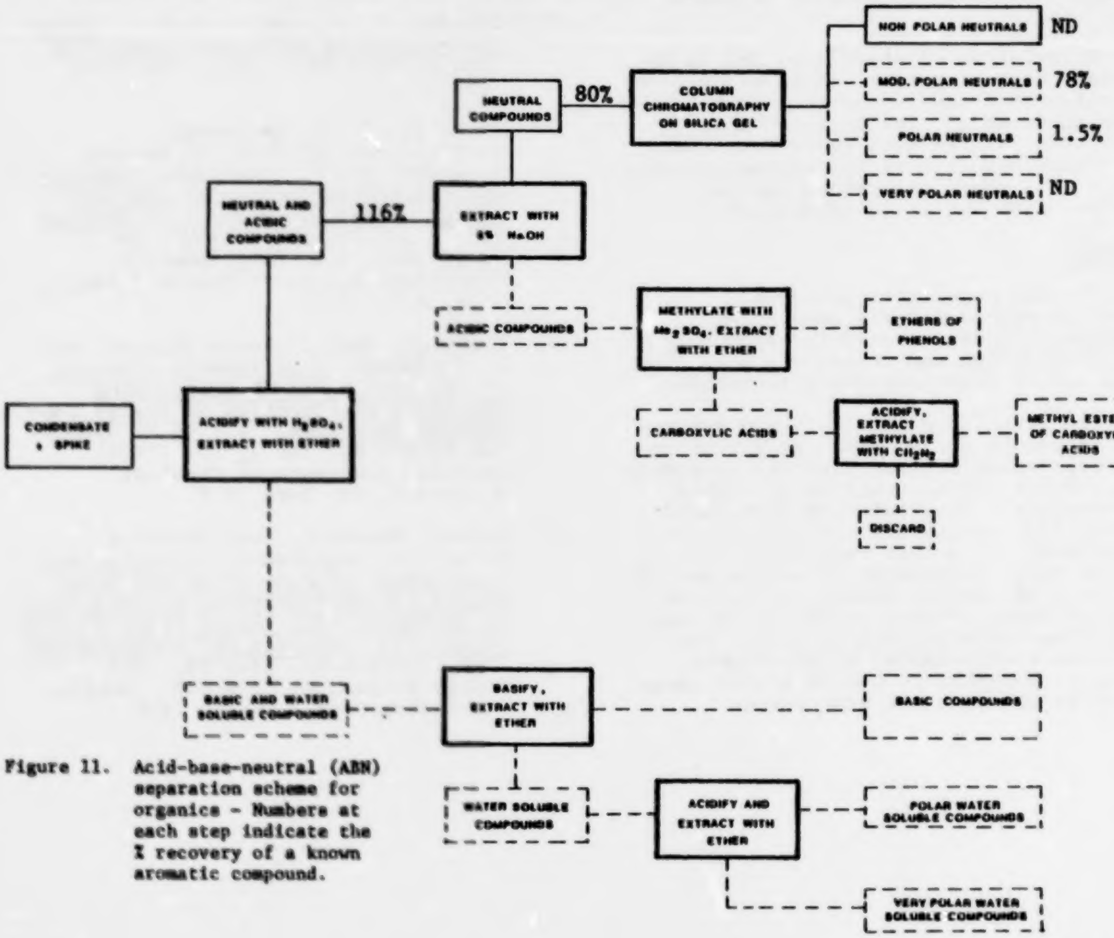
NON POLAR NEUTRALS
ND
NEUTRAL COMPOUNDS
80%
COLUMN CHROMATOGRAPHY ON SILICA GEL
MOD. POLAR NEUTRALS
78%
POLAR NEUTRALS
1.5%
VERY POLAR NEUTRALS
ND
NEUTRAL AND ACIDIC COMPOUNDS
116%
EXTRACT WITH 5% NaOH
ACIDIC COMPOUNDS
METHYLATE WITH Me₂SO₄. EXTRACT WITH ETHER
ETHERS OF PHENOLS
CONDENSATE + SPIKE
ACIDIFY WITH H₂SO₄, EXTRACT WITH ETHER
CARBOXYLIC ACIDS
ACIDIFY, EXTRACT METHYLATE WITH CH₂N₂
METHYL ESTERS OF CARBOXYLIC ACIDS
DISCARD
BASIC AND WATER SOLUBLE COMPOUNDS
BASIFY, EXTRACT WITH ETHER
BASIC COMPOUNDS
WATER SOLUBLE COMPOUNDS
ACIDIFY AND EXTRACT WITH ETHER
POLAR WATER SOLUBLE COMPOUNDS
VERY POLAR WATER SOLUBLE COMPOUNDS

Figure 11. Acid-base-neutral (ABN) separation scheme for organics - Numbers at each step indicate the % recovery of a known aromatic compound.

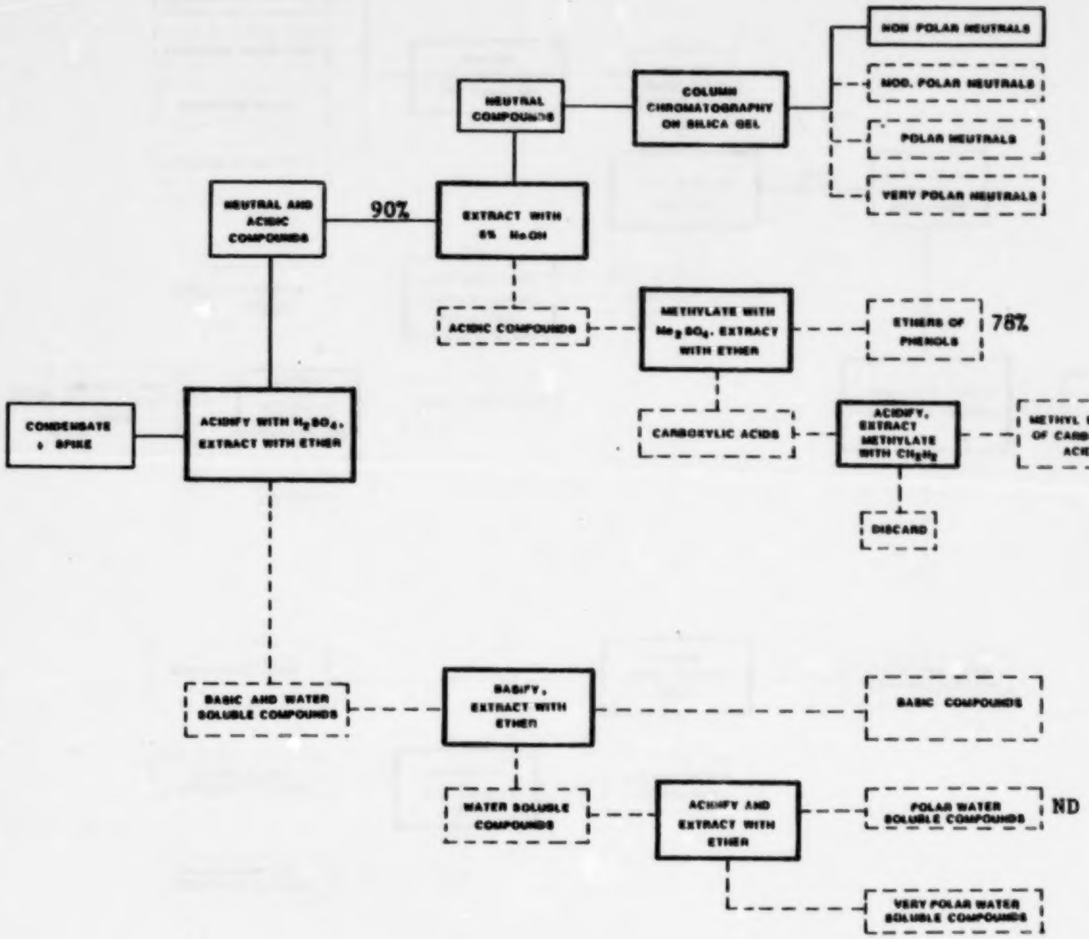
CONDENSATE + SPIKE
ACIDIFY WITH H2SO4, EXTRACT WITH ETHER
NEUTRAL AND ACIDIC COMPOUNDS
90%
EXTRACT WITH 5% NaOH
NEUTRAL COMPOUNDS
COLUMN CHROMATOGRAPHY ON SILICA GEL
NON POLAR NEUTRALS
MOD. POLAR NEUTRALS
POLAR NEUTRALS
VERY POLAR NEUTRALS
ACIDIC COMPOUNDS
METHYLATE WITH Me2SO4, EXTRACT WITH ETHER
ETHERS OF PHENOLS
78%
CARBOXYLIC ACIDS
ACIDIFY, EXTRACT METHYLATE WITH CH2N2
METHYL ESTERS OF CARBOXYLIC ACIDS
3%
DISCARD
BASIC AND WATER SOLUBLE COMPOUNDS
BASIFY, EXTRACT WITH ETHER
BASIC COMPOUNDS
WATER SOLUBLE COMPOUNDS
ACIDIFY AND EXTRACT WITH ETHER
POLAR WATER SOLUBLE COMPOUNDS
ND
VERY POLAR WATER SOLUBLE COMPOUNDS

Figure 12. ANB separation scheme - Numbers at each step indicate the recovery of a known phenolic compound.

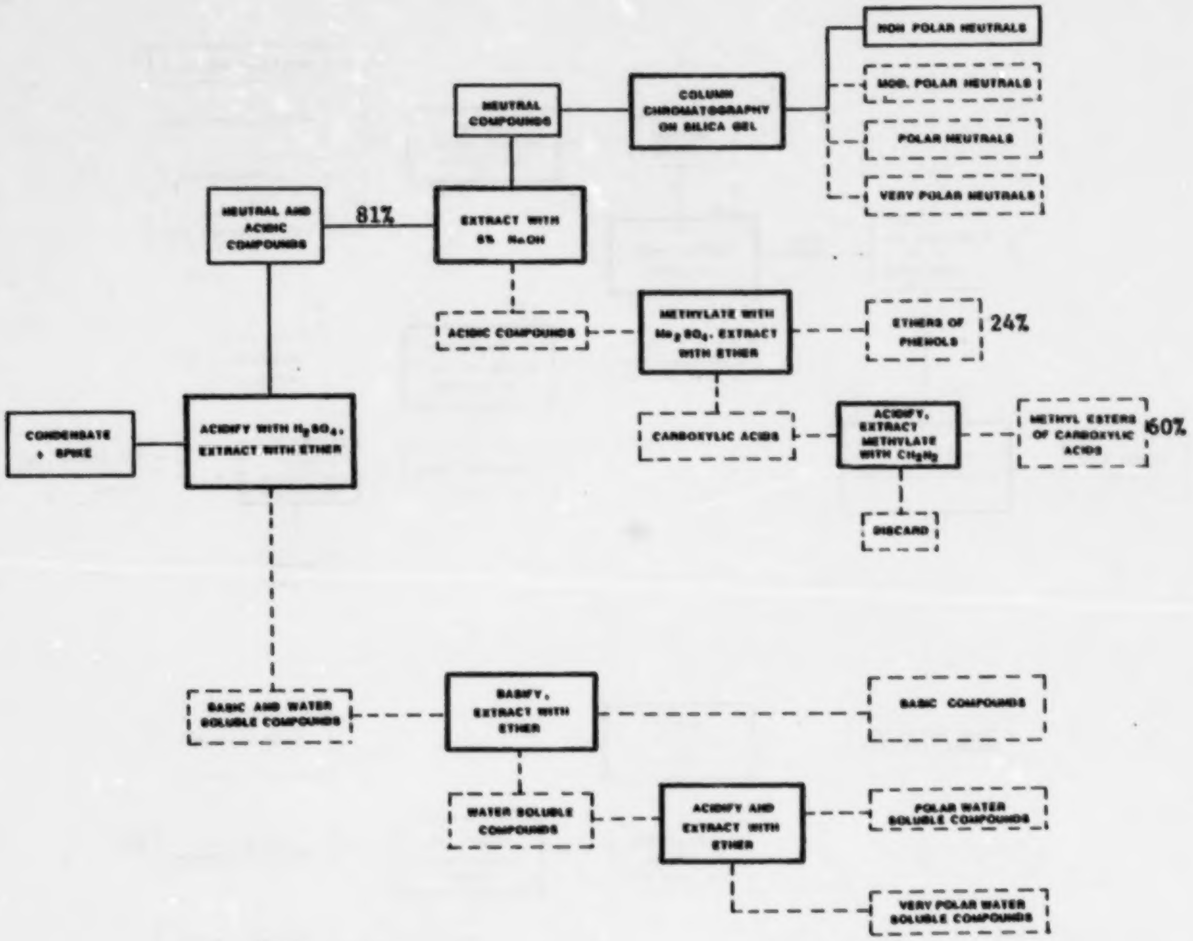
NON POLAR NEUTRALS
NEUTRAL COMPOUNDS
COLUMN CHROMATOGRAPHY ON SILICA GEL
MOD. POLAR NEUTRALS
POLAR NEUTRALS
VERY POLAR NEUTRALS
NEUTRAL AND ACIDIC COMPOUNDS
81%
EXTRACT WITH 5% NaOH
ACIDIC COMPOUNDS
METHYLATE WITH Me_2SO_4, EXTRACT WITH ETHER
ETHERS OF PHENOLS
24%
CONDENSATE + SPIKE
ACIDIFY WITH H_2SO_4, EXTRACT WITH ETHER
CARBOXYLIC ACIDS
ACIDIFY, EXTRACT METHYLATE WITH CH_2N_2
METHYL ESTERS OF CARBOXYLIC ACIDS
60%
DISCARD
BASIC AND WATER SOLUBLE COMPOUNDS
BASIFY, EXTRACT WITH ETHER
BASIC COMPOUNDS
WATER SOLUBLE COMPOUNDS
ACIDIFY AND EXTRACT WITH ETHER
POLAR WATER SOLUBLE COMPOUNDS
VERY POLAR WATER SOLUBLE COMPOUNDS

Figure 13. ABN separation scheme - Numbers at each step indicate the recovery of a known organic acid.

SYNTHETIC FUELS PRODUCTION: ANALYSIS OF PROCESS BY-PRODUCTS FROM A LABORATORY SCALE COAL GASIFIER

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Introduction

A research program is currently in progress at the Research Triangle Institute to investigate the particular pollution problems associated with coal gasification through the construction and operation of a laboratory scale gasifier. This program is funded by EPA/RTP and is moving into its second year. The major goal of the project is the assessment and analysis of trace pollutants possibly associated with the coal gasification process. Such efforts are needed because of the known hazard potential associated with certain materials that are likely to be introduced into the environment from commercial gasifiers. Coal screening studies are being conducted to determine the relationship between various U.S. coals and their pollutant potential. Another important feature of the program is the utilization of the reactor for pollutant control through parametric variation, *i.e.*, the manipulation of operational variables to effect environmental control. A third phase of the project entails a study of gasification kinetics to discern possible relationships between product formation probabilities and process parameters.

The gasifier system has been operational for several months after having undergone several modifications to both the reactor and the sampling train. A schematic of the entire system is depicted in Figure 1. The overall direction of the gasification program, and the operation of the reactor is the responsibility of the Process Engineering Department of the Research Triangle Institute; the analysis of fixed gases and C_1 to C_6 hydrocarbons is accomplished through the Environmental Measurements Department. The analysis of the product gas stream for volatile components, and the analysis of the non-volatile tars and waters are carried out by the Chemistry and Life Sciences Department and these studies form the basis for this presentation.

Analysis

The materials constituting the gasifier by-products are exceedingly complex and represent a formidable task for analysis both qualitatively and quantitatively. Because of the very large numbers of components associated with each sample type, many of which are chemically quite similar, the methodology utilized must possess high resolving power, exhibit a high degree of specificity and be reasonably sensitive. The only tool currently available that provides this combination of features is gc-ms-comp. Use of capillary column technology permits the direct analysis of many samples without the need for extensive prefractionation. This provides an advantage in terms of cost effectiveness that is unrivaled in current analytical practice.

The laboratory gasifier produces two types of samples which are collected and treated by somewhat different procedures. Materials that are carried along with the gas stream after passage through the tar/water trap are termed "volatiles", and are collected by entrapment on polymeric sorbents. Those substances that are knocked out by the tar/ water trap are termed "non-volatile", and consist of the coal tars and condensate water. Each of these samples will be discussed in terms of qualitative analysis followed by a separate discussion regarding quantitative aspects of their analysis.

Volatiles

As can be seen from Figure 1, the volatile materials are removed from the gas stream from two types of sorbents XAD-2 and Tenax GC. The former is used as a means of collecting components during the full course of a gasification run; the latter is utilized as a "grab" device so that samples may be selected at discrete times. Methodology for the analysis of the components adsorbed onto the trap material was borrowed from previous work carried out in our laboratories involving the characterization of gaseous contaminants from air.(1) The method involves the thermal desorption of the adsorbed components from the polymer (Tenax GC) onto a cooled (LN_2) capillary trap. The trap is then rapidly heated to sweep the contents onto a temperature programmed capillary GC system which is interfaced to a continuously scanning mass spectrometer. Mass spectra are thus acquired for each component which, after interpretation provides the identity of each compound. The same characterization process is applied to compounds adsorbed onto the XAD-2 resin, except here the polymer is too unstable for thermal desorption. Instead, solvent extraction (Soxhlet) is used followed by concentration of the extracts and injection onto the gc-ms.

The results of a typical gasification run are depicted in Tables 1 and 2 for volatiles collected onto Tenax and XAD-2. Total ion current (TIC) plots (Figures 2 and 3) depict the elution pattern from the capillary GC system. The identifications of individual components corresponding to the various peaks on the TIC plot are shown on the appropriate list (Tables 1 and 2). Some two hundred compounds are thus collected from the gas stream by both the Tenax and XAD-2. For the most part the materials collected by each sorbent are the same although the amounts collected may differ. This is a reflection of the different selectivities of the two polymers towards various organic species, as well as the effects of varying breakthrough volumes due to the presence of other organics, some of which, for example benzene, are present in relatively large amounts. The major materials identified include saturated and unsaturated hydrocarbons, alkylated aromatics, alkylated phenols, and furan and thiophene derivatives. Alkanes from C_7 to C_{16} are present as are lower condensed ring aromatics upto anthracene. These are the limits on materials found in the gas stream (the gc conditions used for this work are known to elute much higher molecular weight species).

Non-volatiles

The non-volatile materials, i.e., those materials collected in the tar/water trap, represent an exceedingly complex sample for which total methodology is by no means fully developed. Treatment of the condensed waters is reasonably straightforward and consists of solvent extraction, chemical derivatization, and analysis by gc-ms. Using methylene chloride as the extractant, approximately 0.5% (wt./wt.) of the water is removed as organic extractables. This material contains a wide range of compound types with phenolics comprising a large majority. The derivatization is incorporated as a means of converting carboxylic acids (found in very low proportions) and aromatic hydroxyl species to their corresponding methyl derivatives. This vastly improves their gc characteristics and thus eases the mass spectrometric identification and quantification process. Diazomethane is used to convert acids to methyl esters while dimethyl sulfate is preferred for methylation of phenolics. The latter process is fraught with some difficulty in obtaining good yields of derivative; recent efforts in our laboratories have shown that phenol can be converted quantitatively to anisole using high concentrations of base (potassium hydroxide) during this process. The concentrated solution of derivatized material is then injected onto the capillary gc-ms system (Carbowax 20M) and the effluents scanned as described above. Results of this procedure are shown in Table 3 and Figure 4. This data was collected before the completion of the above mentioned dimethylsulfate optimization procedure and hence shows underivatized phenols. As expected, the fraction is relatively rich in those components that possess greater water solubility, i.e., phenols, with lesser amounts of other materials that have been scrubbed from the tars.

The tar fraction represents the most challenging of the samples in terms of analytical treatment. The sheer number of molecular types ranging from highly polar oxygenated species to paraffinic hydrocarbons, and from simple low molecular weight molecules to polymeric material dictates the need for some form of pretreatment before final analysis. We utilize a solvent partition scheme which reduces the tar sample to 5 fractions each of which is enriched in compounds of a similar chemical nature. Each fraction is then either analyzed by the gc-ms or further fractionated using hplc. The solvent partition procedure is a modification of Novotny's method(2) and is depicted schematically in Figure 5. This procedure has been validated through the testing of standard mixtures and by the use of radiolabeled material.

The acid fraction as isolated from the tar sample is very similar in composition to the water extracts described above. Treatment is therefore identical to the latter sample, i.e., derivatization and gc-ms. The organic base fraction is ammenable to direct gc-ms analysis. This fraction is almost entirely composed of heterocyclic amines derived from three aromatic classes; pyridines, indoles, and quinolines. Some higher condensed ring systems are represented as shown in Table 4.

The neutral fraction is conveniently separated by partition into three additional classes, non-polar, (mostly paraffins), PNA's and polar. The latter has not yet been actively investigated. The paraffins have likewise remained unexamined because they are, for the most part, of low environmental hazard potential. Of most interest is the PNA fraction both as a class and individually. Their analysis at this point consists of a direct gc-ms approach. With efficient capillary systems, sufficient resolution of this complex fraction can be achieved with up to five ring molecules eluting within a reasonable time. Results of a typical run are shown in Figure 7 and Table 5. Many of these compounds are of course cancer suspect agents and as such warrant careful examination with regard to the amounts generated during a gasification run. For this reason the quantitative aspects of our work have been directed initially toward the PNA's.

Quantitation

Once the identification process has been completed for a given sample type, the determination of actual quantities of specific compounds or groups of compounds can be undertaken. This process i.e. the quantitation by gc-ms of a relatively few components from a highly complex synfuels sample has not been heavily reported in the open literature. It is not possible therefore to draw on pertinent data produced and published by other workers. The generation of the information necessary for these general quantitation procedures is a consequence only slowly obtained via a step-by-step process that is carried out for each gc-ms system being utilized.

The quantitation process has been described in a recent publication.(3) The method basically involves selected ion monitoring of specific ions of the compounds in question, and comparing the ion intensities of those ion's with a characteristic ion from a carefully chosen internal standard. (The use of peak areas from a gc trace is not feasible due to the complexity of the sample). Using a predetermined response factor, the amount of various components can then be ascertained. The response factor is determined on a molar basis and is reported as a relative molar response (RMR) which is defined as follows:

$$\mathrm{RMR}_{\mathrm{unknown/standard}} = \frac{A_{\mathrm{un}}/\mathrm{moles}_{\mathrm{un}}}{A_{\mathrm{std}}/\mathrm{moles}_{\mathrm{std}}} \qquad (1)$$

where A = peak area obtained from selected ion plots. Thus to determine the RMR, a concentration of unknown and standard must be accurately known and the system response must be measured. Values are determined in replicate. From equation (1) then:

$$g_{\mathrm{un}} = \frac{A_{\mathrm{un}} \cdot \mathrm{GMW}_{\mathrm{un}} \cdot g_{\mathrm{std}}}{A_{\mathrm{std}} \cdot \mathrm{GMW}_{\mathrm{std}} \cdot \mathrm{RMR}_{\mathrm{un/std}}} \qquad (2)$$

where GMW = gram molecular weight of compound. The choice of internal standard will depend on the type of compound being analyzed and should display suitable retention and fragmentation characteristics as well as favorable ionization cross-section. We customarily use perfluorinated or perdeuterated materials, e.g. decadeuteroanthracene for PNA samples.

Several PNA hydrocarbons were chosen as representative of compounds that have been found in coal tar mixtures previously. These materials were then used to calculate RMR's based on the use of decadeuteroanthracene as internal standard. Both a quadrupole and a magnetic sector instrument were used for this study so as to provide a basis for comparing data from two gc-ms systems. Both instruments employed 25M SCOT columns containing OV-101. Data from each system was obtained in a multiple ion detection (MID) mode. Thus a mixture containing known amounts of the chosen PNA's and internal standard was injected onto the gc column and the effluent was monitored by continuous ms scan. Peak areas corresponding to the parent ions of all components were then generated from MID plots and ratioed to the internal standard area. From equation (1) RMR's were then calculated and are shown below in Table 6.

It would seem that the response factors are highly dependent on the particular gc-ms system utilized as there is no discernable correlation between the two sets of data. These factors were then used to calculate the amounts of those chosen PNA's present in the PNA fraction collected from a recent coal gasification run. The MID plots thus generated included several components with the same parent ion as the standard mixture possessed. Selection of the peak corresponding to each of the standards used was made on the basis of relative retention time. With the peak areas of the compounds selected and knowing the molecular weights and area of each compound and the internal standard, the amount of each substance was calculated from equation (2). The results are shown in Table 7.

The agreement between figures from the two systems, while not completely gratifying, is within expectations for the initial applications of the procedure. A crucial experiment yet to be carried out involves the analysis of a sample mixture containing known amounts of materials. This will provide an assessment of the validity of the method and yield information on the magnitude of the errors involved.

The use of RMR's is not restricted to direct application of the type outlined above. More expeditious use of the data would be desirable when large numbers of compounds are to be quantitated. From Table 6 it appears that, for 3 ring systems, the RMR values are reasonably constant. It is possible then that a single, "average" value could be applied to all 3-ring aromatic systems with an acceptable limit of error. Other ring system RMR's might also be obtained for further applications. If, instead of using the parent ion for monitoring and quantitation purposes, an ion that is common to a given ring system were chosen, then a vast amount of quantitative data could be generated from a minimal amount of mass spectral output. An examination of a compound index based on mass spectral fragmentation patterns for a number of PNA's indicates that a common ion approach is not without some potential.

Although only PNA's have been examined thus far, the same procedures will be applied to the other non-volatile fractions as time permits. Studies are already underway for the quantitation of the volatile components, again using the RMR approach.

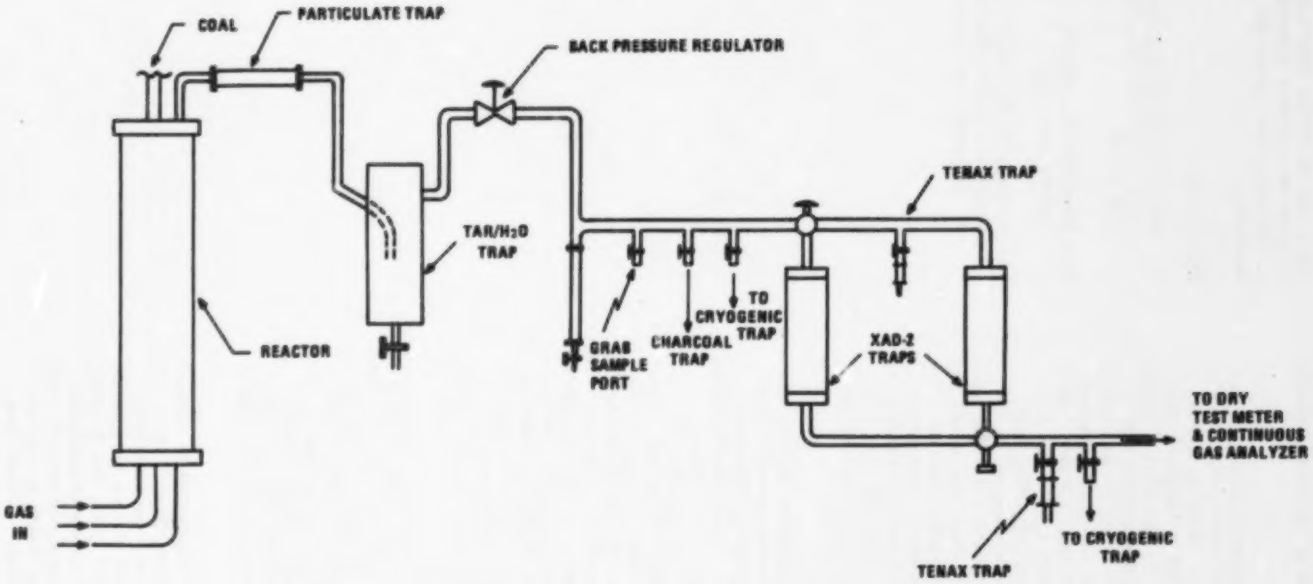
References

1. Pellizzari, E. D., Carpenter, B. H., Bunch, J. E., Sawicki, E., Environ. Sci. Tech., 9, 556 (1975).

2. Novotny, M., Lee, M. L., Bartle, K. D., J. Chrom. Sci., 12, 606 (1974).

3. Bursey, J. T., Smith, D., Bunch, J. E., Williams, R. N., Berkley, R. E., Pellizzari, E. D., American Laboratory, Dec. 1977, p. 35.

Figure 1. Gasifier & Sampling Train


COAL
PARTICULATE TRAP
BACK PRESSURE REGULATOR
TENAX TRAP
TAR/H₂O TRAP
REACTOR
GRAB SAMPLE PORT
CHARCOAL TRAP
TO CRYOGENIC TRAP
XAD-2 TRAPS
TO DRY TEST METER & CONTINUOUS GAS ANALYZER
GAS IN
TENAX TRAP
TO CRYOGENIC TRAP

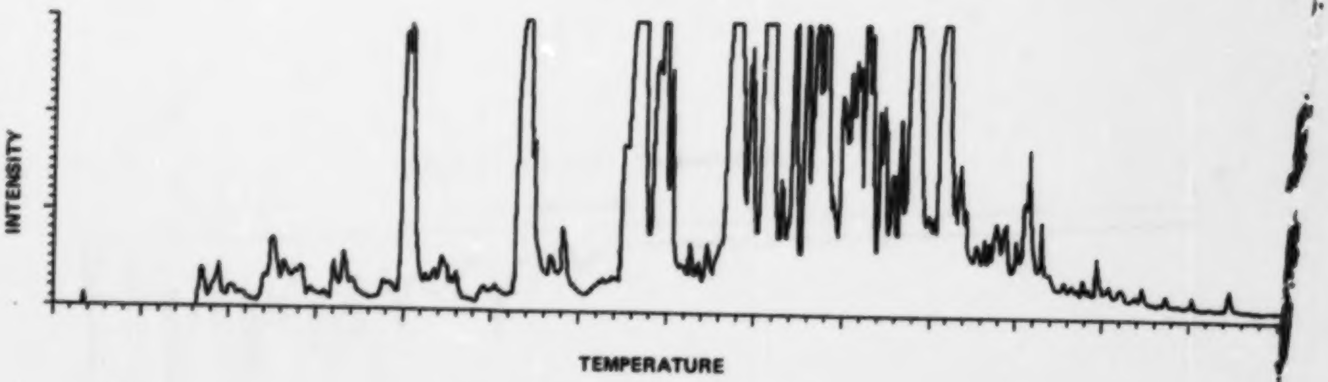


Figure 2. TIC plot. Tenax volatiles.

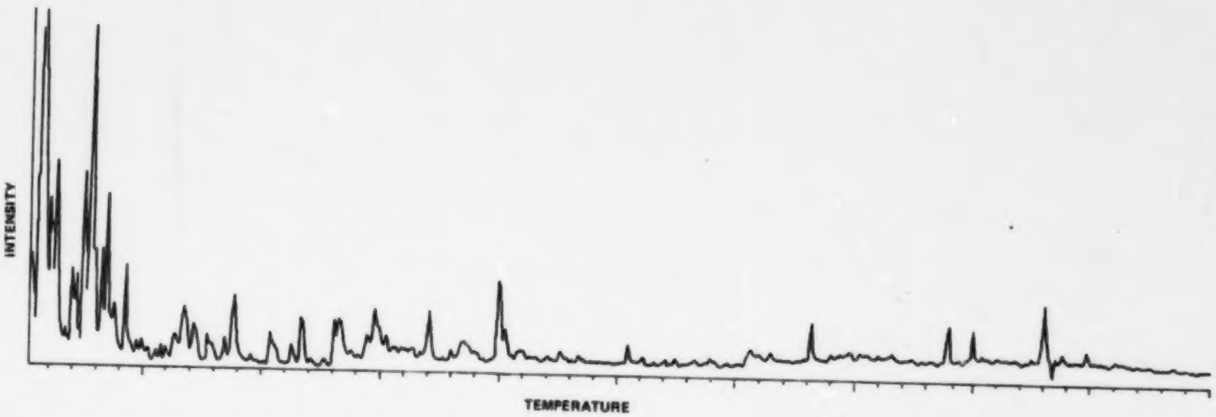


Figure 3. TIC plot. XAD-2 volatiles.

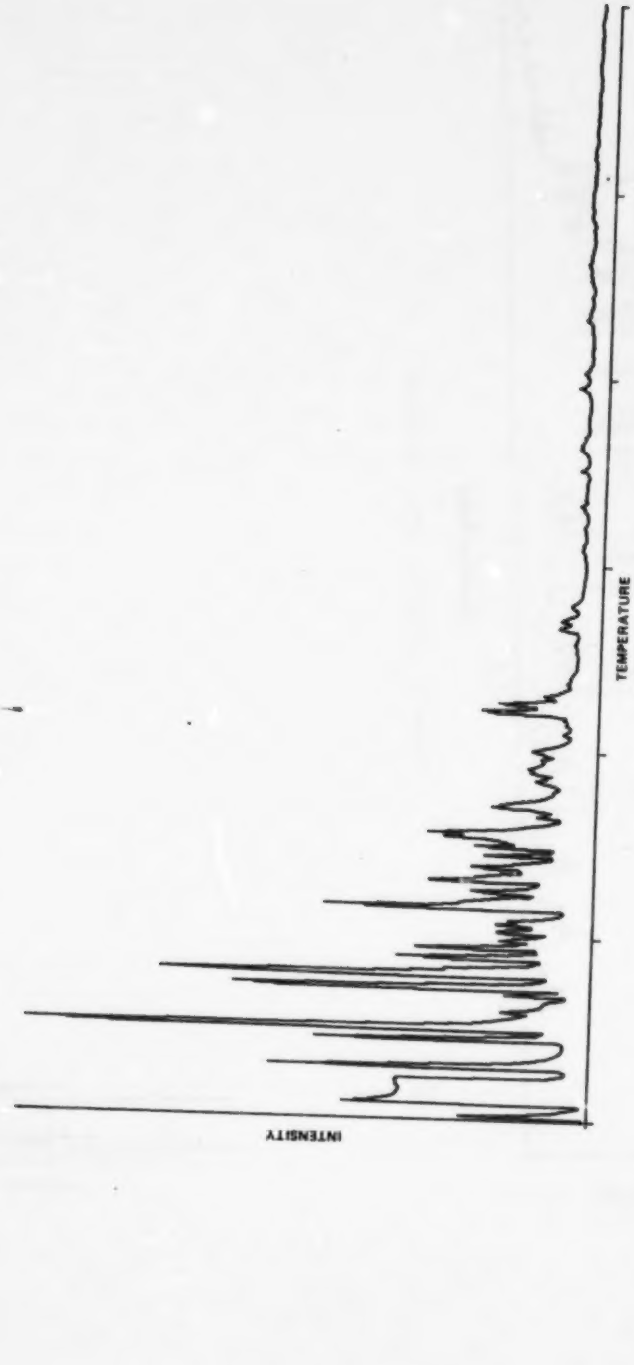


Figure 4. TIC plot. Condensate water.

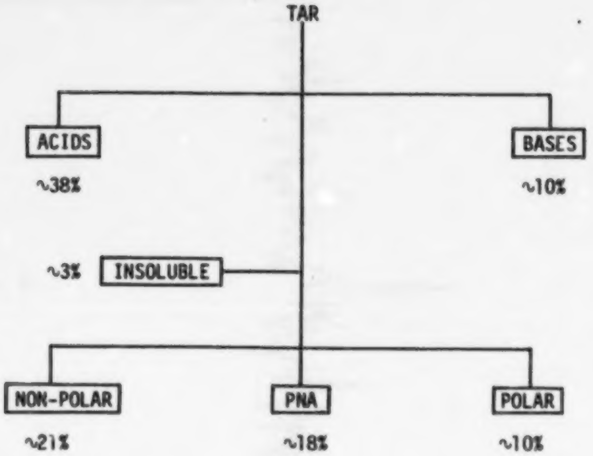

TAR
ACIDS
~38%
BASES
~10%
~3%
INSOLUBLE
NON-POLAR
~21%
PNA
~18%
POLAR
~10%

Figure 5. Solvent partition scheme. Tars.

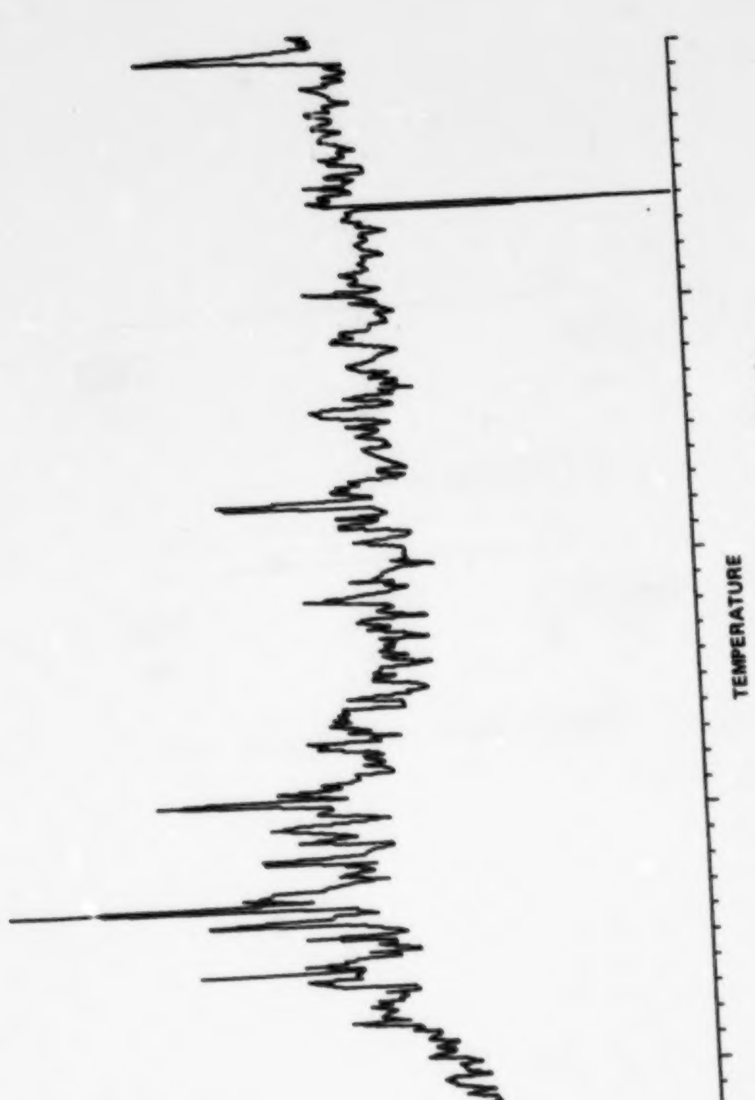


Figure 6. TIC plot. Non-volatiles-organic base fraction.

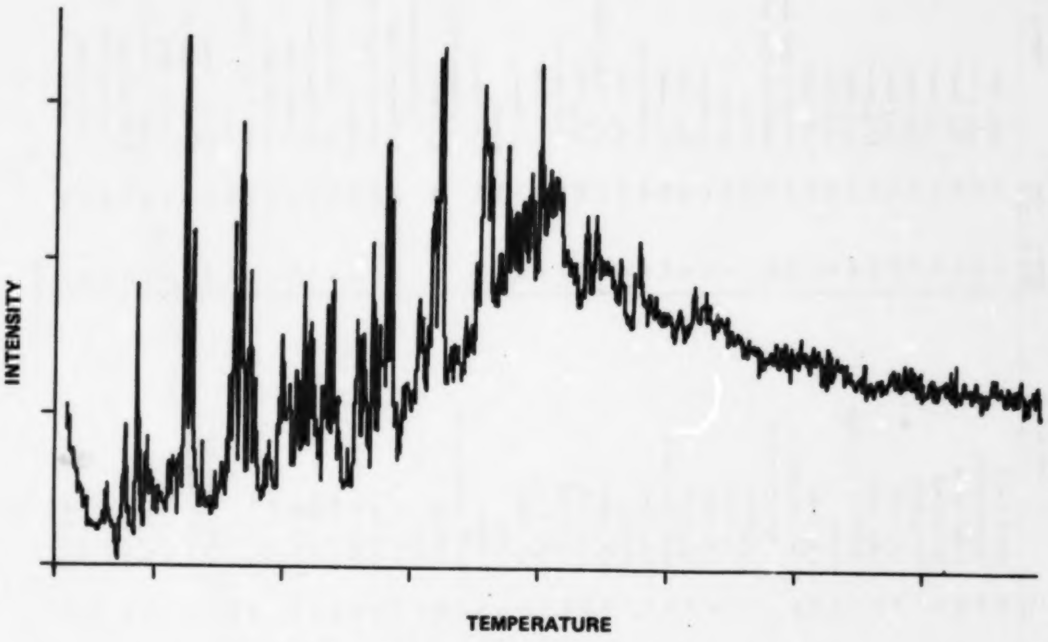


Figure 7. TIC plot. Non-volatiles-PNA fraction.

Table 1. TENAX VOLATILES

Chromatographic Peak No.	Elution Temp. (°C)	Compound
2	48	carbon dioxide
3	50	carbonyl sulfide
4	51	sulfur dioxide
5	53	butene isomer
5a		butene isomer
5b	56	C_5H_{12} isomer
6	57	C_5H_{10} isomer
7	59	unsaturated hydrocarbon
8	61	acetone
9	63	C_5H_{10} isomer
9a	65	carbon disulfide + methylene chloride
10	67	C_5H_6 isomer-
11	68	C_5H_6 isomer
11a	68	C_5H_8 isomer
12	70	C_5H_{10} isomer
13	72	methyl ethyl ketone
13a	72	C_6H_{12} isomer
15	76	_n_-hexane
15a	78	C_6H_{10} isomer
15b	80	C_6H_{12} + C_7F_8 isomers
16	82	C_6H_{12} isomer
17	83	C_6H_{18} isomer
17a	84	C_6H_{10} isomer
18	85	benzene
19	88	thiophene
20	90	methyl isopropyl ketone
21	92	2-pentanone
22	93	trichloroethylene
22a	94	C_7H_{14} isomer
23	95	_n_-heptane
24	96	C_7H_{14} + C_7H_{12} isomers
24a	98	C_7H_{12} isomer
25	102	C_7H_{14} isomer
25a	103	acetic acid
26	103	C_7H_{10} isomer
26a	106	C_7H_{12} isomer
27	108	toluene
27a	110	methylthiophene isomer
28	111	methylthiophene isomer
28a	112	C_8H_{16} isomer
29	113	C_8H_{16} isomer
29a	114	C_8H_{16} isomer
30	115	_n_-octane
30a	116	C_8H_{16} isomer
30b	117	C_8H_{16} isomer
30c	118	C_8H_{14} isomer
30d	120	C_8H_{14} isomer
30e	121	C_8H_{14} isomer
30f	122	C_9H_{20} isomer
30g	122	C_8H_{16} isomer
30h	123	C_8H_{16} isomer
30i	124	C_9H_{18} isomer
30j	125	C_9H_{18} isomer
31	128	ethylbenzene
32	130	xylene isomer
32a	131	dimethylthiophene isomer
32b	132	dimethylthiophene isomer
33	134	styrene
34	135	_o_-xylene
34a	135	C_2-thiophene
35	136	C_9H_{20} isomer
35a	138	C_9H_{18} isomer
36	140	isopropylbenzene
37	141	C_9H_{16} isomer
38	143	C_9H_{18} + $C_{10}H_{22}$ isomers
38a	144	$C_{10}H_{22}$ isomer
39	145	_n_-propylbenzene
39a	146	C_3-thiophene
40	147	C_3-benzene
41	148	phenol
41a	149	C_3-thiophene + C_3-benzene isomers
42	150	C_3-benzene + C_3H_5-benzene isomers
42a	151	C_3-thiophene isomer
43	154	benzofuran + C_3-benzene isomer
43a	155	_n_-decane
44	156	2,3,4-trimethylthiophene
44a	157	C_4-thiophene isomer
44b	158	C_4-benzene isomer
45	159	C_3-benzene isomer
46	161	cresol + C_3H_5-benzene isomers
47	163	indene
47a	163	C_4-benzene isomer
47b	164	C_4-benzene isomer (tent.)
48	165	C_4-benzene isomer
48a	166	cresol + C_4-thiophene isomers
48b	166	C_4-benzene isomer
49	167	C_4-thiophene isomer
50	168	C_4-benzene isomer
50a	166	C_4H_7-benzene

(continued)

Table 1 (cont'd)

Chromato- graphic Peak No.	Elution Temp. (°C)	Compound
51	169	C_4-benzene isomer
51a	170	C_4H_7-benzene
52	170	$C_{11}H_{22}$ isomer
52a	171	C_2-phenol
53	171	methyl benzofuran isomer
53a	171	$C_{11}H_{24}$ isomer
54	172	methyl benzofuran isomer
54a	173	C_4-benzene
55	173	C_5-benzene + $C_{11}H_{22}$ isomers
56	175	C_4-benzene isomer
57	176	C_4H_7-benzene isomer
58	177	C_2-phenol isomer
58a	178	C_5-benzene isomer
59	179	C_4H_7-benzene isomer
59a	179	C_5-benzene isomer
59b	179	C_4-thiophene isomer
59c	180	ethylphenol isomer
60	181	methyl indene isomer
60a	181	C_4H_7-benzene isomer
60b	181	C_4-benzene isomer
60c	181	methyl indene isomer
61	182	C_5-benzene isomer
62	184	C_2-phenol isomer
62a	184	C_5H_9-benzene isomer
63	186	benzoic acid
63a	187	C_5H_9-benzene isomer
64	187	naphthalene
64a	187	C_5H_9-benzene isomer
64b	188	2,3-benzothiphene + *n*-dodecane + C_5-benzene isomer
64c	188	C_5H_9-benzene isomer
65	188	dimethylbenzofuran isomer
66	189	$C_{13}H_{28}$ isomer
67	190	dimethylbenzofuran isomer
68	191	C_6-benzene isomer
69	193	C_5H_9-benzene isomer
70	195	methyl dihydronaphthalene isomer
71	196	C_5H_9-benzene isomer
72	197	methyl dihydronaphthalene isomer
72a	198	C_5H_9-benzene isomer
73	199	$C_{14}H_{30}$ isomer
73a	199	$C_{12}H_{16}$ isomer
74	201	$C_{13}H_{26}$ + C_5H_9-benzene isomers
74a	202	$C_{14}H_{28}$ + methylbenzothiophene isomers
75	202	tridecane
76	203	β-methylnaphthalene
76a	204	C_6H_{11}-benzene isomer
76b	204	methylbenzothiophene isomer
77	206	α-methylnaphthalene
77a	207	C_6H_{11}-benzene isomer (tent.)
78	210	C_6H_{11}-benzene isomer
79	211	$C_{14}H_{30}$ isomer
80	214	$C_{15}H_{32}$ isomer
80a	214	hydrocarbons
81	216	*n*-tetradecane
81b	216	ethylnaphthalene isomer
82	218	dimethylnaphthalene isomer
83	220	dimethylnaphthalene isomer
84	224	dimethylnaphthalene isomer
85	225	$C_{16}H_{34}$ isomer + biphenylene
85a	226	C_2-naphthalene isomer
86	229	*n*-pentadecane + acenaphthene
86a	232	C_3-naphthalene isomer
87	236	dibenzofuran or $C_{12}H_{18}O$ + C_8H_{15} benzene isomers
87a	237	C_3-naphthalene isomer
87b	239	C_3-naphthalene isomer
88	240	2,2,4-triethyl penta-1,3-diol di-isobutyrate

Table 2. XAD-2 VOLATILES

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound	Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1a	70	C_7H_{14} isomer + C_8H_{14} isomer	21a	70	C_3-alkyl benzene isomer
1b	70	C_7H_{10} isomer	21b	70	C_3-thiophene + $C_{10}H_{20}$ isomer
1c	70	C_8H_{16} isomer	22a	70	C_3-alkyl benzene isomer
2	70	toluene* + C_7H_{12} isomer	22b	70	C_3-thiophene isomer
2a	70	methyl thiophene isomer	22c	70	$C_{10}H_{18}$ isomer
3a	70	cyclooctane or C_8H_{16} isomer	22d	70	$C_{10}H_{20}$ isomer
3b	70	C_8H_{14} isomer	23	70	C_3-alkyl benzene isomer
4a	70	n-octane	24a	70	C_3-thiophene isomer
4b	70	C_8H_{16} isomer	24b	70	$C_{10}H_{20}$ isomer
4c	70	C_8H_{14} isomer	24c	70	$C_{10}H_{18}$ isomer
4d	70	C_9H_{18} isomer	25a	71	benzofuran
4e	70	octyne isomer	25b	71	methyl styrene isomer
5a	70	C_8H_{14} isomer	26a	72	C_3-alkyl benzene isomer
5b	70	C_9H_{18} + C_9H_{16} isomers	26b	73	$C_{10}H_{20}$ isomer
6a	70	C_8H_{16} + C_9H_{20} isomers	26c	74	$C_{10}H_{18}$ isomer
6b	70	C_8H_{14} isomer	27a	76	$C_{10}H_{20}$ isomer
6c	70	trimethylcyclohexane isomer	27b	77	$C_{10}H_{20}$ isomer
7	70	C_8H_{14} + C_9H_{18} isomers	27c	77	trimethylthiophene isomer
8a	70	ethylbenzene	27d	78	C_4-alkyl benzene isomer + unsaturated hydrocarbons
8b	70	dimethylthiophene isomer			
9a	70	dimethylbenzene isomer	27e	78	$C_{10}H_{20}$ isomer
9b	70	C_8H_{14} isomer	27f	78	unsaturated hydrocarbons
10a	70	C_9H_{20} + C_9H_{18} + C_9H_{16} isomers	28a	79	n-decane
10b	79	styrene + C_2-thiophene isomer	28b	80	1,2,3-trimethylbenzene
11a	70	C_2-alkyl benzene isomer	28c	81	C_4-alkyl benzene isomer
11b	70	C_9H_{18} isomer	28d	81	C_4-alkyl benzene isomer (tent.)
12a	70	C_9H_{16} isomer	29	82	indan
12b	70	C_9H_{18} isomer	30	85	indene
12c	70	C_9H_{16} isomer	31a	87	2-methyldecane
13a	70	n-nonane	31b	87	$C_{10}H_{20}$ isomer
13b	70	C_9H_{18} isomer	31c	87	$C_{11}H_{20}$ isomer
13c	70	C_9H_{16} isomer	32a	88	diethyl benzene isomer*
13d	70	C_9H_{18} + $C_{10}H_{20}$ isomers	32b	88	C_4-alkyl benzene isomer
14	70	isopropylbenzene + $C_{10}H_{20}$ isomers	33	90	C_4-alkyl benzene isomer
15a	70	C_9H_{16} isomer	34a	91	C_4-alkyl benzene isomer
15b	70	C_9H_{18} isomer	34b	92	cresol isomer + C_4-thiophene isomer (tent.)
16	70	C_9H_{16} isomer			
17a	70	C_9H_{18} isomer	35a	93	C_4-alkyl benzene isomer
17b	70	$C_{10}H_{20}$ isomer	35b	93	$C_{11}H_{20}$ isomer (tent.)
18	70	$C_{10}H_{20}$ + $C_{10}H_{18}$ isomers	35c	94	C_4-thiophene isomer
19a	70	$C_{10}H_{22}$ isomer	35d	94	unsaturated hydrocarbons
19b	70	$C_{10}H_{22}$ isomer	36	95	C_4-alkyl benzene isomer
20a	70	C_3-alkyl benzene isomer	37a	95	C_4H_7 benzene isomer
20b	70	$C_{10}H_{22}$ isomer	37b	96	C_4-alkyl benzene isomer
20c	70	isopropylthiophene isomer	37c	97	cresol isomer

(continued)

Table 2 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
37d	97	saturated hydrocarbons
38a	98	C_4H_7 benzene isomer*
38b	91	cresol isomer + $C_{11}H_{20}$ isomer
39	100	methylbenzofuran isomer
40a	101	C_2-phenol isomer
40b	102	methylbenzofuran isomer
40c	102	unsaturated hydrocarbons
40d	102	C_5-alkyl benzene isomer
40e	102	$C_{11}H_{24}$ isomer
41	103	$C_{11}H_{22}$ benzene
42a	104	C_4H_7 benzene isomer*
42b	105	C_4-alkyl benzene isomer
42c	106	n-undecane
42d	107	$C_{12}H_{22}$ isomer
43a	109	C_4H_7-benzene isomer
43b	109	C_5H_9-benzene
43c	110	C_5-alkyl benzene isomer
44a	111	methylindene isomer*
44b	111	C_4H_7-benzene isomer
44c	111	C_5-alkyl benzene isomer
44d	112	methylindene isomer
44e	112	C_4-alkyl benzene isomer
45a	113	C_2-phenol isomer
45b	114	$C_{12}H_{24}$ isomer
45c	115	C_5-alkyl benzene isomer
46a	116	C_5-alkyl benzene isomer
46b	118	naphthalene
47a	119	benzothiophene isomer
47b	119	$C_{12}H_{22}$ isomer (tent.)
47c	120	C_2-phenol isomer + unknown
47d	120	C_5H_9-benzene isomer
47e	120	$C_{12}H_{26}$ isomer + C_5H_9-benzene isomer
48a	121	C_6-alkyl benzene isomer*
48b	122	$C_{12}H_{22}$ isomer*
48c	123	C_5H_9-benzene isomer
48d	123	C_5-alkyl benzene isomer
49a	124	C_6-alkyl benzene isomer
49b	124	$C_{12}H_{24}$ isomer
50a	125	$C_{12}H_{22}$ isomer
50b	126	dimethylbenzofuran isomer + hydrocarbons
51a	128	$C_{12}H_{26}$ isomer
51b	129	C_6-alkyl benzene isomer
51c	129	C_5H_9-benzene isomer
52a	130	$C_{13}H_{28}$ isomer
52b	131	$C_{13}H_{26}$ isomer
52c	133	C_6-alkyl benzene isomer
52d	134	$C_{11}H_{12}$ isomer
53	138	C_6H_{11} benzene isomer
53	139	methylnaphthalene isomer
54	142	methylnaphthalene isomer
55a	145	unsaturated hydrocarbons
55b	145	$C_{14}H_{28}$ isomer + $C_{14}H_{26}$ isomer
55c	146	$C_{13}H_{28}$ isomer
55d	146	$C_{12}H_{16}$ isomer
56	147	unknown
57a	149	$C_{14}H_{26}$ isomer
57b	150	$C_{13}H_{20}$ isomer
58a	152	$C_{14}H_{26}$ isomer
58b	152	biphenyl
58c	155	$C_{14}H_{26}$ isomer
58d	158	$C_{14}H_{26}$ isomer
58e	158	dimethylnaphthalene isomer
59	160	$C_{14}H_{22}$ isomer (tent.) + dimethylnaphthalene isomer
60	162	n-tetradecane
61a	163	C_2-naphthalene isomer
61b	164	acenaphthylene
61c	165	unsaturated hydrocarbon
61d	166	C_2-naphthalene isomer
62a	169	$C_{12}H_{10}$ isomer
62b	170	C_2-biphenyl isomer*
63	174	dibenzofuran
64	177	$C_{16}H_{30}$ isomer + hydrocarbons
65a	179	$C_{16}H_{30}$ isomer
65b	180	unsaturated hydrocarbons
66	182	unsaturated hydrocarbons
67a	183	methylacenaphthylene isomer
67b	183	diacetyl-6-hydroxybenzofuran or unknown
67c	187	$C_{16}H_{28}$ isomer
67d	187	C_3-biphenyl isomer
67e	189	$C_{17}H_{34}$ isomer + $C_{17}H_{32}$ isomer
68	193	$C_{16}H_{18}$ isomer (tent.)
69a	197	$C_{16}H_{18}$ isomer (tent.)*
69b	202	alkyl benzene
70b	208	anthracene
71a	212	$C_{18}H_{22}$ isomer
71b	212	$C_{18}H_{22}$ isomer
71c	213	$C_{15}H_{28}$ isomer

(continued)

Table 2 (cont'd)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
72a	216	$C_{18}H_{28}$ isomer
72b	217	unknown + $C_{13}H_{22}$ isomer*
72c	217	alkylbenzene

Table 3. CONDENSATE WATER

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
4	70	phenol
5a	72.8	o-cresol
5b	73.2	p-cresol
6	75.6	m-cresol
8	82	o-ethylphenol
9a	83.6	2,5-dimethylphenol
9b	84.4	2,3-dimethylphenol
12	88	naphthalene
13	89.2	3,4-dimethylphenol
15	92.4	1-(p-methyoxyphenol)-1-propanol
16	93.6	4-methyl-2-ethylphenol
17	96.4	1,4,6-trimethyl-2-pyridone
18a	98	3-methyl-6-ethylphenol
18b	98.4	2-methyl-4-ethylphenol
19a	102.4	p-(2,2,3,4-tetramethylbutyl)-phenol or p-(1,1,3,3-tetramethylbutyl)-phenol
20	102.8	1-methylnaphthalene
21a	105.2	2-methylnaphthalene
21b	105.6	benzothiazole
23a	109.6	dimethylisopropylbenzene isomer
23b	110	5,6,7,8-tetrahydroquinoline
24a	117.2	1- or 2-ethylnaphthalene
25	118.8	dimethylnaphthalene
27	124.0	biphenylene
29	129.2	acenaphthene
30	133.2	2-isopropylnaphthalene
31	134	dibenzofuran
32	135.2	phenylphenol
35	142.8	fluorene
37	145.6	diphenylmethane
39	150.4	hydroxyfluorene
43	159.2	3,4-dimethoxyacetophenone
45a	164.4	xanthone
45b	165.2	3,3'-dimethyl-4,4'-bipyridyl or 2,2'-dimethyl-4,4'-bipyridyl or 2'-hydroxydibenzofuran dibenzo-p-dioxan
45c	166.4	2-diphenylfluorene 2,4,7-trimethyl-1,8-naphthyridine
45d	166.8	benzidine
45e	167.2	2,5-di-nor-heptylthiophene
46a	168	anthracene
46b	168.4	phenanthrene
47a	173.6	dimethylfluorene
47b	174.4	carbazole
47c	175.2	phenanthridone
48a	177.2	1-methoxyphenazine
48b	178.8	3-amino-9-ethylcarbazole
48c	179.6	2,3-dihydro-2-methyl-4-(org)-phenylbenzofuran
48d	182.0	1-amino-7-methylphenazine
48e	182.4	2-methylthio-5-aminothiazolo-(5,4)-pyrimidone
49	183.2	methylanthracene
50a	184.4	methylphenanthrene
50b	184.8	4,5-methylenephenanthrene
51a	185.6	2-phenylindole
51b	189.6	methylcarbazole
51c	190.8	hydroxyanthraquinone
51d	199.2	dimethylphenanthrene
52	200	1-phenylphthalazine
53a	201.2	pyrene
53b	201.6	fluoranthene
53c	206	1,1-dimethylinden
54a	206.8	tetrahydrofluoranthene
54b	212.8	trimethylphenanthrene
54c	214.8	tetrahydroanthraquinone 4,9-dimethylnaphtho-(2,3)-bithiophene
54d	218	methylpyrene isomer
54e	227.2	6-acetylnaphthazarin
54f	233.6	benzanthone
54g	244.4	triphenylene

Table 4. ORGANIC BASE FRACTION

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	103.2	pyridine
2	113.6	N-methyl-o-toluidine or 4-acetyl pyridine
3	117.2	4-acetyl pyridine
4	121.8	quinoline butiodide
5	125.6	2,6-dimethyl-4-ethyl pyridine
6	131.6-139.6	6-methyl quinoline
7	140.0	3- or 4-methyl quinoline
8	141.2	2-amino-5-chloro-4,6-dimethyl pyrimidine
9	143.6	8-nor-propyl quinoline
10	144.8	ethyl quinolines or 2-amino-5-chloro-4,6-dimethyl pyrimidine
11	147.2-153.6	2,6-dimethyl quinoline
11	147.2-153.6	ethyl quinolines
12	154.4	3,5,5-trimethyl-1-hexanol
13	156	4-ethyl quinoline
14	157	2,6-dimethyl quinoline
14	157	3-nor-propyl quinoline
15	160.4	4-phenyl-2-pyridone
16	162	4-phenyl-2-pyridone
16	162	2,6-dimethyl quinoline
17	164.4	1,2,3,4-tetrahydrocarbazole
18	166.2	4- and 6-phenyl-2-pyridone
18	166.2	ethyl quinoline
19	168	methyl-3-allylindolenine
20	170	4-nor-propyl qunioline
20	170	3-methyl-3-allylindoline
21	172.8	3-methyl-3-allylindoline
22	175	3-methyl-3-allylindoline
22	175	4-phenyl-2-pyridone
23	177.8	diphenyl amine
24	178.8	2-amino-4-phenyl-6-methyl pyrimidine
24	178.8	phenyl-2-pyridone
25	179.8	2,2'-dimethyl-4,4'-dipyridyl
26	192	N-methyl carbazole
27	193.8	2-methyl carbazole
28	197.4	benzo(h)quinoline
29	198	acridine or benzo(h)quinoline
30	200.4	benzo(h)quinoline
30	200.4	3-amino-9-ethyl carbazole
31	207.2	3-amino-9-ethyl carbazole
32	210	3-methylbenzoquinoline
33	210.8	3-amino-9-ethyl carbazole
34	216.4	3-methylbenzoquinoline
34	216.4	3-amino-9-ethyl carbazole
34	216.4	benzo(h)quinoline or acridine
35	221,2	3- and 5-methyl-2-phenylindole
36	224	3- and 5-methyl-2-phenylindole
37	226.4	3-methylbenzoquinoline
38	228.6	3- and 5-methyl-2-phenylindole
39	234.4	fluoranthrene
39	234.4	3-methylbenzoquinoline
39	234.4	3- and 5-methyl-2-phenylindole
40	238.4	4-styrylquinoline
40	238.4	3- and 5-methyl-2-phenylindole
41	239.6	3-benzylindene phthalimidine
41	239.6	3-methylbenzoquinoline
41	239.6	3- and 5-methyl-2-phenylindole
42	246	4-(1,2,3,4-tetrahydro-2-naphthyl)-morpholine
43	261.6	3,4-diphenyl pyridine
44	265	dibutyl phthalates
45	265	di-2-ethylhexylphthalate

Table 5. NON-VOLATILES - PNA FRACTION

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	116.8	methyl phenyl acetylene?
2	123.6	4-methylbenzo(b)furan
3	129.8	methyl indenes
4	133.6	naphthalene
4	134.4	2,3-dihydro-2-methylbenzofuran
5	136.8	1-hydroxy-2-methyl-4-ethylbenzene?
5	136.8	o-hydroxyacetophenone?
6	138.8	1-methyl-4-nor-hexyl-1,2,3,4-tetrahydronaphthalene
7	150.4	2-methylnaphthalene
8	152.0	1-methylnaphthalene
9	164.8	ethylnaphthalene
9	164.8	2,3-dimethylbenzo(b)thiophene
10	166.4	methylnaphthalene isomers
11	168.8	1,5- and 2,3-dimethyl naphthalene
12	172.0	1,3-dimethylnaphthalene
13	173.6	1,2-dimethylnaphthalene
14	177.6	acenaphthene or biphenyl
14	177.6	methylbiphenyl isomer
15	180.8	2-ethyl-5(or 7)-methylbenzo (b) thiophene
15	180.0	2-i-propylnaphthalene
16	181.6	dibenzofuran
19	187.2	propylnaphthalene
20	189.6	fluorene
22	192.8	1,3-dihydro-4,6-dimethylthieno (3,4-c)thiophene
23	194.4	2-methylbiphenyl
24	197.6	2-hydroxyfluorene
25	198.4	2-tert-butylnaphthalene
27	202.4	1-methyl-7-iso-propylnaphthalene?
28	209.6	1-methylfuorene
29	212.8	methoxyfluorene isomer
30	215.2	methoxyfluorenes or ortho- and para-phenylanisole
32	224.0	dimethylfluorene
33	229.6	3-methyldibenzothiophene
34	231.2	phenyl x-xylyl ketone?
35	236.0	methylphenanthrene
36	239.2	2-methylcarbazole
38	242.4	tetrahydroanthraquinone?
39	244.0	4,5-dimethyl-9,10-dihydrophenanthrene?
40	248-252.0	dimethylphenanthrenes
42	255.2	8-nor-butyl-phenanthrene?
43	256.0	ethylanthracene
44	257.6	pyrene
45	260.8	1-methylbenzo(1,2-b:4,3-b)-dithiophene
46	263.2	hexadecapyrene?
47	264.0	trimethylphenanthrene?
48	265	1-methylpyrene
49	265	trimethylphenanthrene
50	265	trimethylphenanthrene
50	265	1,4-dimethylanthracene
51	265	1,2,3,4-tetrahydrotriphenylene
51	265	1,4-dihydro-2,3-benzcarbazole
52	265	tetrahydrotriphenylene
52	265	dihydrobenzcarbazole
52	265	4,4'-dichlorobiphenyl?
53	265	tetrahydrotriphenylene
53	265	dihydroxyanthraquinone
54	265	butyl phthalyl butyl phthalate
54	265	3-nor-hexylperylene?
54	265	3,6-dimethyoxyphenanthrene
55	265	3,3'-bi-indolyl
55	265	4,4'-dichlorobiphenyl
56	265	1,2-diphenylbenzene
57	265	1,4-diphenylbenzene
58	265	1,3-diphenylbenzene
59	265	hexahydrobenz(a)anthracene
60	265	diphenylbenzene
61	265	triphenylene?
62	265	di-nor-octylphthalate
62	265	di-2-ethylhexylphthalate
63	265	methylbenzo(a)anthracene or 3-methylchrysene or 2-methyltriphenylene
64	265	5-methylbenzo(a)anthracene?
65	265	9-,10-, or 11-methylbenz(a)-anthracene
66	265	perylene? or benzpyrene?
67	265	benzpyrene or perylene
68	265	3-methylacenaphthylene

Table 6. RELATIVE MOLAR RESPONSE

Compound	RMR (Mag. Sector)	RMR (Quadrupole)
Naphthalene	42.51	1.48
2-Methylnaphthalene	4.31	1.00
Fluorene	2.81	1.16
Phenanthrene	1.28	1.26
Anthracene	1.41	1.80
9-Methylanthracene	1.32	.91
Fluoranthene	1.87	1.61
Pyrene	2.35	1.78
Chrysene	15.64	.74

Table 7. PNA QUANTITATION

Compound	Found (Mag. Sector)	Found (Quadrupole)
Naphthalene	25.5 ng	-
2-Methylnaphthalene	45.4	85.2
Fluorene	13.9	33.7
Phenanthrene	61.4	36.9
Anthracene	57.4	29.7
9-Methylanthracene	76.0	48.4
Fluoranthene	12.4	5.2
Pyrene	14.7	8.0
Chrysene	11.3	-
Perylene	10.4	-

TRANSFORMATION OF POM IN POWER PLANT EMISSIONS

by

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Abstract

With the advent of increased usage of coal as an energy source, environmental considerations must be examined. It has been known that fossil fuels produce organic emissions commonly known as Polycyclic Organic Matter (POM) which constitute a health threat in that some POM show a high degree of carcinogenic activity. In this paper some aspects of POM transformations will be examined which include the mode of transformation, reactions which are believed to occur in the environment, the environmental ramifications of POM transport, and the associated considerations of sample collection, theoretical models, laboratory experiments, and emission controls.

Introduction

During the last several years there has been increasing recognition of the importance of polycyclic organic matter (POM) as an air pollutant.(1) This is largely due to the increasing weight of circumstantial evidence which relates the incidence of certain types of cancers (notably bronchial carcinoma) to atomspheric levels of POM - especially benzo(a)pyrene.(1-4) Recently, an amendment to the 1970 Clean Air Act(5) has recognized POM as a potential hazard to health. Whether this hazard is substantiated or not it is reasonable to expect an increase in POM sampling and analysis activities in the future. Consequently, it is appropriate at this time to consider some of the factors which determine the authenticity of POM measurements.

Specifically, it is the purpose of this paper to point out that many of the compounds which are classified as POM can undergo both physical and chemical transformations. These transformations can, it is suggested, profoundly influence the meaning and validity of POM measurements, the environmental impact of POM, and the applicable control technology.

There is now a considerable body of evidence(1) which shows that POM formation occurs as a result of combustion of carbonaceous material, that formation is promoted by reducing conditions, and that similar relative amounts of individual compounds are produced irrespective of the nature of the fuel. Most of the information available concerns the polycyclic aromatic hydrocarbons (PAH), though it is recognized that polycyclic aromatic compounds containing both hetero-atom rings and ring substituents are produced.(1)

The detailed mechanism(s) of POM formation are not well understood; however, it is widely accepted that POM is formed via a free radical mechanism(6) which occurs in the gas phase. As a result POM originates as a vapor. On the other hand, there is a large body of data which attests to the fact that POM present in the atmosphere is almost invariably found in particulate form.(1) It is apparent, therefore, that vapor-to-particle conversion takes place between the points of formation of POM in a combustion source and its determination in the atmosphere. It is the mechanism of this vapor-particle transformation and the subsequent oxidative transformation of particulate POM which constitute the subject of this paper.

Vapor-Particle Transformation

A number of workers have reported the presence of vapor phase POM in combustion sources where elevated temperatures are encountered.(7-10) In most cases, however, particulate POM is present at much higher levels than vapor phase POM, indicating that the process of vapor-to-particle conversion is both rapid and, eventually, quantitative.

The most obvious mechanisms of vapor-to-particle conversion of POM involve condensation or nucleation of POM vapor and adsorption of POM onto the surface of co-existing particulate matter. While both processes may operate, it is pointed out that the POM vapor pressures encountered in most combustion sources are simply not high enough for condensation or nucleation to occur.(7-12) In other words, the saturation vapor pressure or dew point of POM must be attained for these processes to take place.(13) Such levels may possibly occur in special instances such as during a so-called "green push" from a coke oven.(1)

On the other hand, adsorption of POM vapor onto the surface of particulate material present in stack or exhaust gases can certainly take place and could account for the almost exclusive occurrence of particulate POM at ambient atmospheric temperatures. In order to investigate the possible operation of an adsorption mechanism we are currently conducting a study which involves theoretical modelling, field measurement, and laboratory simulation experiments. These are described briefly, together with the preliminary results, in the following sections.

Theoretical Model

Our theoretical model is designed to consider the active adsorption of POM (primarily PAH's) from the vapor phase onto the surface of particulate material (coal fly ash) as the two move down a nonuniform temperature gradient (the stack system). The treatment is, however, quite general and applies to any vapor species and any particulate adsorbant.

The basic assumption is that a given POM, P, present in the vapor phase, can adsorb onto the surface, S, of particulate material to provide an adsorbed entity, P.S, and that the reverse process can also take place. Thus,

$$P + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P\cdot S \qquad (1)$$

where k_1, k_{-1} are the rate constants for adsorption

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**Present address: Universidade Campinas, Sao Paulo, Brazil and desorption, respectively. If one assumes, *a priori*, that k_1 and k_{-1} in equation (1) represent first-order processes, then the rate of adsorption of P can be written

$$\frac{d[P\cdot S]}{dt} = k_1[P](1-\theta)A - k_{-1}[P\cdot S] \qquad (2).$$

In equation (2), θ is the fraction of the total available adsorption sites which are occupied and A is the surface area of the particulate material.

The rate constant for desorption, k_{-1}, is given by

$$k_{-1} = \frac{kT}{h}\exp\left[-E_d/RT\right] \qquad (3)$$

where E_d is the activation energy for desorption, T is the absolute temperature, and k, h and R are Boltzmann's constant, Planck's constant, and the universal gas constant, respectively. The rate constant for adsorption, k_1, is

$$k_1 = c\left[\frac{RT}{2\pi M_a}\right]^{1/2}\exp\left[-E_a/RT\right] \qquad (4)$$

where c is the so-called "sticking coefficient" (the probability that the orientation of a molecule with the spherical particle surface will result in adsorption), M_a is the molecular weight of the adsorbate species, and E_a is the activation energy for adsorption. A number of assumptions are inherent in equations (3) and (4). These are presented briefly in reference (14) and discussed in detail in a forthcoming publication.(15)

In order to evaluate the rate and extent of adsorption as a function of temperature it is convenient to compute the mole fraction, X, of total POM adsorbed and the time taken to achieve one half of the equilibrium adsorption at a given temperature, $t_{1/2}$. The equations giving these quantities are:(14,15)

$$1/X = 1 + \frac{(2\pi M_a k)^{1/2}}{6cw_p h}\,\frac{d_m^3}{d_s^2}\,\frac{\rho\, T^{1/2}\exp\,(E_a-E_d)/RT}{1-\theta \quad N_0^{1/2}} \qquad (5)$$

and

$$t_{1/2} = \frac{-1}{k_1\gamma+k_2}\ln\frac{(2-X)k_1\gamma - Xk_2}{2k_1\gamma} \qquad (6)$$

where

$$\gamma = (1-\theta)\,\pi\left[\frac{d_m^3}{d_s^2}\right]^2, \text{ and } N_0 = 6.02 \times 10^{23}.$$

The quantities ρ and W_p are, respectively, the density and mass per unit volume of the adsorbing particles and d_m and d_s are the mass and surface median diameters, respectively, of the particle size distribution. In the case of a log Gaussian distribution of particle sizes d_m and d_s are related by

$$\ln d_s = \ln d_m - \ln^2\sigma \qquad (7)$$

where σ is the geometric standard deviation of the distribution.(16)

The evaluation of equations (5) and (6) requires that realistic values be chosen for the quantities c, M_a, w_p, ρ, d_m^2/d_s^2, E_a, E_d, and θ. In fact the fractional surface coverage, θ, is almost certainly dependent on both temperature and the values of E_a and E_d; however, it is reasonable to assume that the adsorption process is zeroth order in θ so that a constant value can be chosen. Using available literature values for the above parameters (given in figure captions) one can construct the temperature dependent plots of X and $t_{1/2}$ presented in Figures 1 and 2.

Consideration of the data presented in Figure 1 shows that, over a wide range of conditions, POM present at combustion source temperatures (>150°C) is predicted to occur mainly in the vapor phase, whereas at the ambient temperatures encountered following emission (<40°C) essentially quantitative adsorption is predicted. Variations from this general behavior are, however, predicted for individual compounds and widely different particle size distributions and mass loadings.

The temperature dependencies shown in Figure 1 are generated with the assumption that adsorption equilibrium is achieved at all temperatures. This requires that the rate of attainment of equilibrium is fast compared with the rate of change of temperature experienced by a given vapor-particle combination. The rate of attainment of equilibrium is indicated in terms of the half-time for reaction in Figure 2. These data show that reaction times depend primarily on the activation energies E_a,E_d in equations (3) and (4) and that achievement of sub-second reaction times at both in-stack and ambient temperatures requires activation energy values to be at the lower end of the range investigated. Indeed, reduction of the activation energy for adsorption by only a few kcals results in achievement of equilibrium within a few seconds even at ambient temperatures.

While the foregoing brief discussion is far from rigorous or conclusive, it does validate the possibility of vapor-to-particle conversion of POM occurring via an adsorption mechanism. Further, it points out the very strong temperature dependence of such a process.

Field Measurements

In order to investigate the occurrence of vapor-to-particle conversion occurring in a combustion source, measurements were made in the stack system and in the emitted plume of a small coal fired power plant. This plant was specially chosen because it was of obsolete design utilizing a chain grate stoker known to produce high POM emissions;(12) it possessed no particle control equipment, thereby facilitating collection of large amounts of particulate material; and it had a relatively short stack such that sample collection from the emitted plume was possible.

Fly ash samples were collected during the same time periods both inside the stack (temp. ~290°C) and from the emitted plume (temp. ~5°C) using both cascade impaction and total collection on glass fiber filters. Collected material was extracted with benzene and analyzed for POM using GC, GC-MS, and fluorimetry. All necessary analytical precautions were taken and it was established that material collected from the plume was derived exclusively from the power plant.

The results of these analyses are presented in Tables 1 and 2 which list the individual compounds uniquely identified and provide a quantitative measure of the specific concentrations (μg/g) of several compounds associated with fly ash at the two sampling points. Preliminary identification was established using GC retention time data and in many cases was confirmed using either a single-ion mass chromatogram or a mass spectrum from a GC peak. Only crude vapor traps were employed during sample collection so no quantitative measure of vapor phase POM was obtained. Fluorescence measurement of condensation trap residues did, however, indicate that a considerable quantity of POM was present from in-stack sampling but none was in residues from plume sampling.

These results establish quite firmly that, in this power plant, considerably more POM is associated with fly ash collected from the plume at a temperature of 5°C than with that collected from the same stream at a temperature of 290°C. This behavior is in exact accord with that predicted in Figure 1. Furthermore, since the two collection points were only ~100 ft apart, quite rapid vapor-to-particle conversion is indicated. Unfortunately while the full range of aerodynamic equivalent particle sizes accessible to Anderson Stack and Hi Vol samplers was collected, this only represented a small range of specific surface area due to the considerable particle irregularity encountered. Nevertheless correspondence between specific concentration of POM and specific surface area of fly ash fractions was noted. This further suggests the operation of a surface adsorption mechanism.

Laboratory Experiments

In an attempt to obtain direct measurements of the rate and extent of POM adsorption and to evaluate the quantities c, E_a, E_d in equations (3) and (4), a series of laboratory simulation experiments were set up. Fresh coal fly ash which had previously been shown to contain no detectable POM was presented in an expanded bed through which a stream of air containing pyrene vapor(17) was passed. The objective was to expose all particles to the same constant concentration of pyrene for different times and to determine the specific concentrations of pyrene as a function of time at different temperatures.

The experiments showed that the uptake of pyrene was so rapid that a uniform vapor phase concentration could not be achieved. The amount of pyrene required to saturate the fly ash was, however, shown to increase significantly with decreasing temperature. Futhermore, attempts to remove adsorbed pyrene by heating in a stream of clean air were unsuccessful.(18)

While these experiments were essentially qualitative they do establish the facts that coal fly ash will strongly adsorb pyrene (and probably other POM) and that the saturation capacity is a strong inverse function of temperature.

Overall, therefore, the results of these three studies point strongly towards the idea that POM, formed initially as vapor, is adsorbed onto co-entrained particulate material as the temperature falls. There is some doubt about the rate at which this process takes place but the evidence is in favor of rapid (on the order of seconds) adsorption, even at ambient temperatures, under most conditions encountered in or near combustion sources.

Oxidative Transformation

It is widely accepted that POM present in atmospheric aerosols is highly susceptible to photochemical transformation in the presence of sunlight. Indeed, several studies of POM, or of individual polycyclic compounds, present on substrates such as airborne particles, soot, and alumina(1) have shown that conversion to an oxidized form occurs quite readily. Yet, if one subjects the available information to critical examination it is apparent that, while photochemical transformations undoubtedly occur, there is considerable disagreement regarding the behavior of different compounds on different substrates.

Our own studies have been designed to establish the factors which determine the rate and extent of photochemical transformation of individual polycyclic aromatic hydrocarbons present on the surface of coal fly ash. Samples have been prepared by adsorbing individual species from the vapor phase(17-19) onto POM-free fly ash which is then subjected to irradiation in the form of sunlight and of several sunlight-simulating ultraviolet sources. Surprisingly, these experiments showed no evidence of photochemical transformation of the compounds employed (Table 3) even though long irradiation times and unrealistically high irradiation intensities were employed. Since these compounds were rapidly transformed in solution one concludes that association with the fly ash surface stabilizes them against photochemical transformation.

Even though photochemical transformations were not observed, several of the compounds studied did undergo partial oxidation simply as a result of being adsorbed onto fly ash (Table 3). In passing, most, but not all, of these reactive compounds possessed at least one benzylic or doubly-benzylic methylene, which is highly susceptible to oxidation. This non-photochemical oxidation process was found to depend greatly on the nature of the adsorbing substrate. Thus, fly ash and activated carbon were found to promote oxidation whereas silica, alumina and glass did not.(19)

While highly preliminary, these results do suggest that certain polycyclic aromatic species undergo oxidation as a result of adsorption onto active substrates. In all cases the extent of conversion was less than 100 percent and the half times for conversion varied from a few minutes to several hours. The tentative conclusion, therefore, is that a number of compounds present in so-called POM can be oxidized both in the presence and absence of light and that this behavior is greatly influenced by the nature of the substrate with which a compound is associated.

Overall, it is apparent that both photochemical and non-photochemical conversion of particulate associated POM is a complex and ill-defined process and merits considerable futher investigation.

Ramifications of POM Transformation

The types of transformation discussed above, while far from definitive, do point out several important considerations which should be borne in mind in assessing the environmental/health impact and methodology for the measurement and control of POM. These may be categorized as follows:

Environmental Considerations

From the standpoint of the environmental and potential human health impact of POM two points are important. The first is that adsorption of vapor phase POM onto particulate matter will result in the predominance of POM on small particles which provide the largest available surface area per unit mass. Thus, POM will be preferentially concentrated in particles whose aerodynamic size falls in the range which can remain airborne for several days and which is capable of being deposited in the pulmonary region of the human respiratory system when inhaled.(20,21) This prediction is in accord with the results of measurements of the atmospheric aerosol size distribution of POM.(21)

The second point to be noted is that, due to the demonstrated photochemical and nonphotochemical transformation of POM, several of the compounds which are present in inhaled aerosols may be significantly different from those actually measured in, and emitted from, a given combustion source. Present indications are that the initial stable conversion products of PAH's are their corresponding ketones and quinones which apparently exhibit lower carcinogenic activity than their parent compounds. However, it is appropriate to recognize that the enhancement or reduction of carcinogenic activity associated with POM is still an entirely open question.

Sample Collection

If POM is capable of converting rapidly from vapor to particulate form then the relative amounts of each would be expected to vary with the position (i.e. temperature and particle surface density) in a combustion system. Consequently, measurements of separate vapor and particulate POM will apply only to a specific point in a specific plant operated under specific conditions and cannot be extended to other power plants in general. Furthermore, the predictions of Figures 1 and 2 suggest that considerable vapor-to-particle conversion may actually occur within the sampling device — especially when it is maintained at a temperature which is different from that of the stream being sampled. As a result measurements of the particle size distribution of POM and of the ratio of particulate to vapor phase POM will not represent true quantities but rather sampling artefacts.

Of more practical importance, however, is the very clear need to collect both vapor and particulate POM in order to establish total POM emission factors. Current methodology for sampling emission sources does employ vapor collection devices; however, some doubt has been expressed concerning their collection efficiency,(22) and it seems likely that present POM emission estimates may be low where measurements are made at elevated temperatures. Certainly emission estimates based on analyses of particulate material alone, when it is collected from within an emission source, are likely to be grossly in error.(23)

Finally, it will be noted that the non-photochemical oxidation observed for POM adsorbed on fly ash is unlikely to occur to the same degree in adsorbent vapor phase POM collectors. Consequently the compounds identified in vapor collection devices may differ considerably from those emitted from a source — certainly the relative concentrations may differ. In short, the material collected may differ qualitatively and quantitatively from that emitted.

Overall, therefore, it seems that the transformation processes discussed herein may result in extremely poor representation of emitted POM unless special sampling precautions are taken. Indeed, the only *bona fide* way of characterizing POM emissions would be to collect material directly from the emitted plume. Since this is unrealistic for routine measurements, it is recommended that emphasis be placed on the determination of total POM under conditions which promote particle association prior to sample collection. For this purpose it is suggested that the sampling train be operated at or below ambient temperatures.(24)

Emission Control

The vapor-to-particle transformation behavior of POM has two important consequences in terms of emission control. First, the fraction of the total POM which is in the vapor phase during passage through particle control devices will not be collected. Secondly, the effect of adsorption is to move the aerodynamic equivalent mass median diameter of the adsorbed species to a value which is significantly smaller than that of the substrate particle mass as described by equation (7). Just as this enhances the ability of POM to penetrate the human respiratory system so it will also increase the difficulty of controlling POM emissions since small particles in the range of interest (0.1 to 5.0 μm aerodynamic diameter) are collected with reduced efficiency by most particle control devices.(25)

One positive point which can be made is that collection of POM vapor by scrubbers may be quite efficient insofar as the low temperatures encountered in liquid systems may promote adsorption and at least partial collection of vapor species.

Conclusion

It is apparent from the foregoing discussions that transformation of POM from vapor to particulate form and to different molecular forms can take place within a combustion source, during sampling, and following sample collection. Indeed a number of chemical transformation processes in addition to those discussed have been reported.(1) It is also apparent that such transformations can profoundly influence the meaning and validity of POM measurements, the environmental impact of POM, and the applicable control technology.

Finally, it is important to recognize that the processes described herein, although presented in terms of a coal-fired power plant, will occur quite generally. They must, therefore, be taken into account when considering any combustion source.

Acknowledgements

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TABLE 1. INDIVIDUAL POLYCYCLIC AROMATIC COMPOUNDS IDENTIFIED* IN EMITTED COAL FLY ASH

Fluorene**
Phenanthrene**
Anthracene**
9,10-dimethylanthracene**
Fluoranthene**
Triphenylene**
Pyrene**
Chrysene**
Benzofluorene
1-methylpyrene
Benzophenanthrene**
Benzo(a)anthracene
Perylene**
Benzo(a)pyrene**
Benzo(e)pyrene**
Benzo(ghi)perylene
Anthanthrene
Coronene

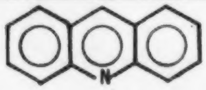
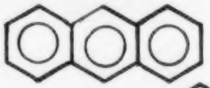
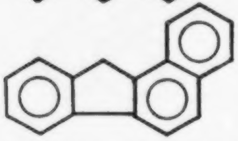
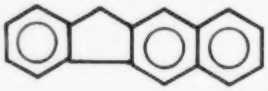
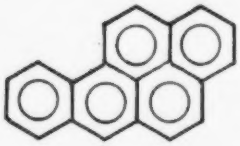
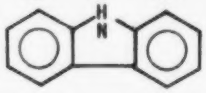
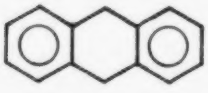
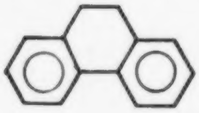
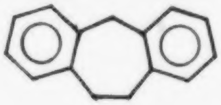
* By gas chromatography or literature data (NAS 1972, Hangebrauck et al., 1967).

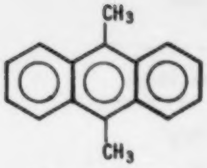
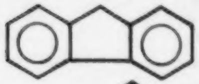
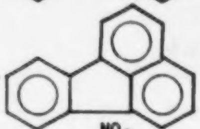
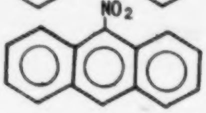
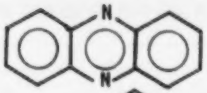
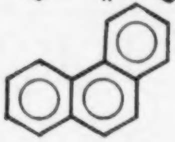
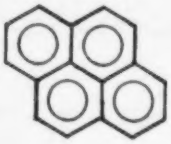
**Identity confirmed by GC/MS using reconstructed ion chromatograms.

TABLE 2. MEASUREMENT OF POM EMITTED FROM COAL FIRED POWER PLANT STACK

Compound	Inside Stack	Outside Stack
Fluorene	ND	0.5 μg/g
Phenanthrene	ND	12
Fluoranthene	ND	17
Pyrene	ND	12
Benzofluorene	ND	2
1-methylpyrene	ND	0.6
Benzophenanthrene	ND	3
Benzo(a)pyrene	ND	8
Total fluorescence/g	$3.61(10^{-3})$ units	3.68 units

TABLE 3. OXIDATION OF POM ADSORBED ONTO FLY ASH SURFACES

Compound		Surface Oxidation	Product
Acridine		No	--
Anthracene		Yes	Anthraquinone
Benzo(a)fluorene		Yes	?
Benzo(b)fluorene		Yes	?
Benzo(a)pyrene		No	--
Carbazole		No	--
9,10-dihydroanthracene		Yes	?
9,10-dihydrophenanthrene		Yes	?
10,11-dihydro-5H-dibenzo-[a,d]-cycloheptane		No	--

9,10-dimethylanthracene		**Yes**	**"Quinone"**
Fluorene		**Yes**	**Fluorenone**
Fluoranthene		**No**	**--**
9-nitroanthracene		**Probably**	**?**
Phenazine		**No**	**--**
Phenanthrene		**No**	**--**
Pyrene		**No**	**--**

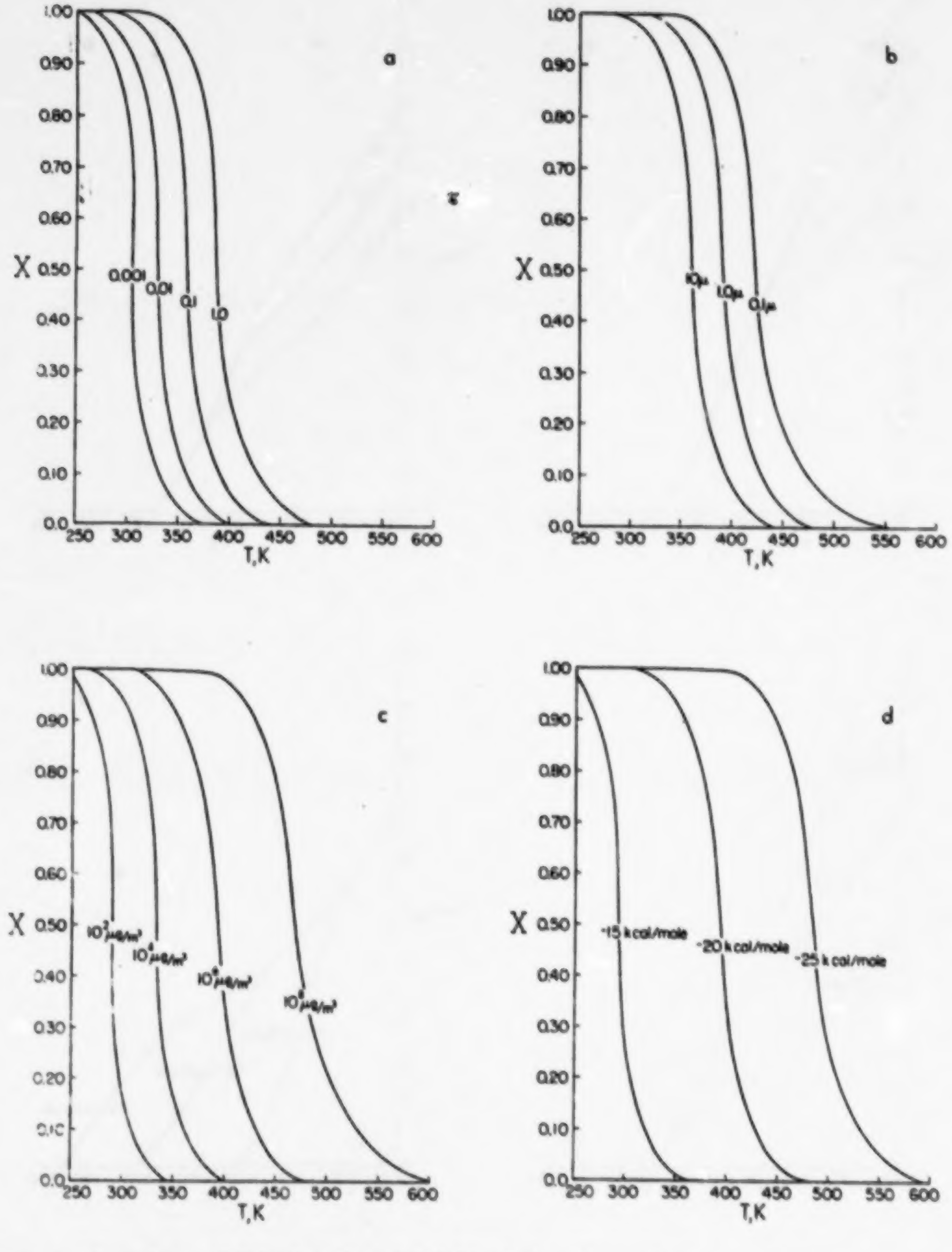


Figure 1. Dependence of Mole Fraction of PAH Adsorbed on Temperature

Reference values: $c = 1$; $m_a = 3.360\ (10^{-22})$ g/molecule; $w_p = 10^6\ \mu g/m^3 = 10^{-6}\ g/cm^3$; $\rho = 3\ g/cm^3$; $d_m{}^3/d_s{}^2 = 10^{-4}$ cm; $E_a = -10$ kcal/mole; $E_d = -30$ kcal/mole; $\theta = ½$.

(a) Variation of mole fraction of PAH adsorbed as a function of temperature and $C = 0.001, 0.01, 0.1, 1.0$.

(b) Variation of mole fraction of PAH adsorbed as a function of temperature and $d_m{}^3/d_s{}^2 = 0.1, 1.0, 10.0$ μm.

(c) Variation of mole fraction of PAH adsorbed as a function of temperature and $w_p = 10^2, 10^4, 10^6, 10^8$ μg/m .

(d) Variation of mole fraction of PAH adsorbed as a function of temperature and E_a-E_d = -15, -20, -25 kcal/mole; $E_a = -10$ kcal/mole.

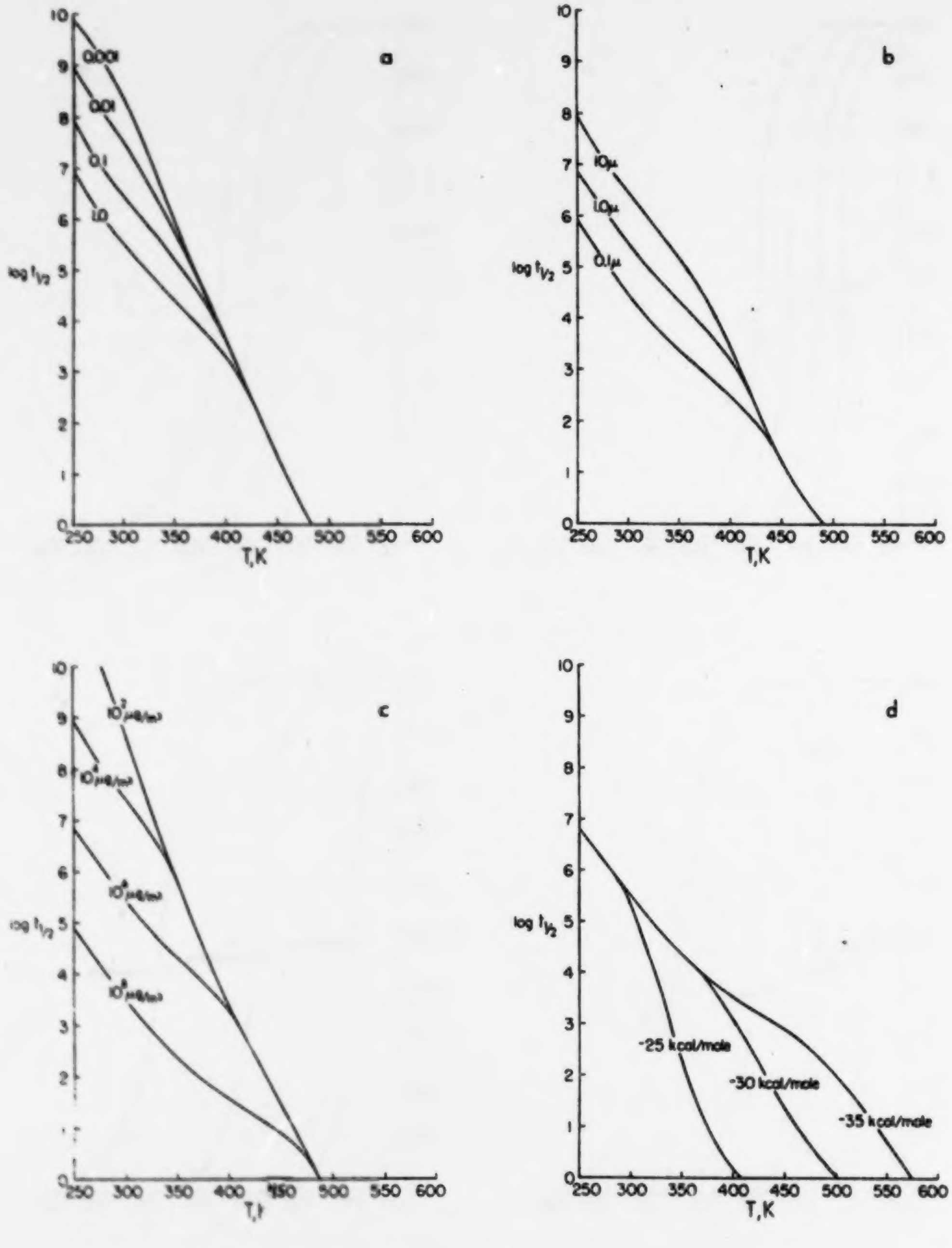


Figure 2. Dependence of Half-time for Adsorption on Temperature

Reference values: c = 1; m_a = 3.360 (10^{-22}) g/molec; w_p = 10^6 μg/m³ = 10^{-6} g/cm³; ρ = 3 g/cm³; d_m^3/d_s^2 = 10^{-4} cm; E_a = -10 kcal/mole; E_d = -30 kcal/mole; θ = ½.

(a) Dependence of half-time for adsorption on temperature and C = 0.001, 0.01, 0.1, 1.0.
(b) Dependence of half-time for adsorption on temperature and d_m^3/d_s^2 = 0.1, 1.0, 10.0 μm.
(c) Dependence of half-time for adsorption on temperature and w_p = 10^2, 10^4, 10^6, 10^8 μg/m³.
(d) Dependence of half-time for adsorption on temperature and E_d = -25, -30, -35 kcal/mole.

THE ASSESSMENT OF ATMOSPHERIC EMISSIONS FROM PETROLEUM REFINING

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Abstract

A study, funded by the U. S. EPA, is currently being conducted in order to assess the atmospheric emissions from petroleum refining operations.

To accomplish this assessment measurements of fugitive hydrocarbon and stack emissions are being made at a number of refineries throughout the country. Sources being sampled include valves, flanges, pumps and compressor seals, process drains, pressure relief devices, process vents, heater and process stacks, cooling towers, API separators, dissolved-air flotation units, open ditches, barometric sumps and holding ponds.

This paper describes the methods being employed for the selection and screening of the above sources and the criteria used for making the sample - no sample decision.

Introduction

The program that Radian undertook for the EPA has three objectives:

- to provide data which can be used for "offset calculations" (This involves the development of emission factors for the various sources in a refinery.);
- to provide a data base for health effects use (This involves the qualitative and quantitative measurement of potentially hazardous components of refinery emissions.); and
- to assess the availability and effectiveness of control technology (This involves the collection of data regarding both controlled and fugitive emissions.).

Pollutants emitted into the air from a refinery fall into one of two categories:

- controlled emissions, or
- fugitive emissions.

The first type is released into the air at a controlled rate from a point source such as a stack or a vent. The second is released without control of rate or direction. Many types of fugitive emissions cannot be measured by existing standard sampling and analytical techniques. Therefore, development of reliable measurement procedures is an essential prerequisite to the development of strategies for the control of fugitive emissions.

The decision to emphasize fugitive emissions in our current study is the result of discussions with the API and the EPA. The interest of the API stems from a need within the refining industry to have access to updated emission factors. The interest of EPA stems from its charge to develop adequate control technology for potentially hazardous pollutants and from a need for emission factors accurate and current enough to allow offset changes to be made in existing refining operations. The most cost-effective program combines elements of both fugitive and nonfugitive source sampling.

Previous studies (1958) have dealt with total hydrocarbon emissions and with emissions of other criteria pollutants. This study considers total and nonmethane hydrocarbons but does not include other criteria pollutants except from nonfugitive sources where current data are not available. The present study also seeks to characterize the individual compounds being emitted which may be potentially hazardous even at trace levels.

The makeup of a "refinery" is difficult to define since the process units employed are dependent on the demands for the refinery's products. Therefore, a test plan was developed that is not definition limited.

Approach

The type and arrangement of process units within refineries may vary considerably from one location to another; however, the individual unit fittings and processes contained in each refinery should show close similarities.

The unit fittings, ranging from valves, pumps, etc., to various seals, are available to industry in a smaller number of varieties than the varieties which may result from the various arrangements of the unit fittings to give unit processes. These fittings largely control the amount of fugitive emissions potentially available from a given unit process.

Thus, the approach is to experimentally determine the emissions from unit fittings. These data will allow calculation of the emission factors as well as calculation of the fugitive emission potential of individual unit processes.

In the case of operations involving fugitive emissions other than those from unit fittings, special sampling approaches have been devised to allow measurements or estimation of the total emissions from those operations.

Sources of Hydrocarbon Emissions

There are several known sources of hydrocarbon emissions in a refinery; they are listed in Table 1.

TABLE 1. REFINERY HYDROCARBON EMISSION SOURCES

Process Emissions Sources:

- Compressor Engines
- Catalytic Cracker Regeneration Stacks
- Air Blowing
- Boilers and Process Heaters
- Flares and Blowdown Systems*
- Vacuum Jets (Vented to the Atmosphere)
- Sulfur Recovery or Tailgas-Treating Unit Stacks

Fugitive Emissions Sources:

- Pipeline Valves
- Miscellaneous Joints
- Pressure-Relief Devices
- Pump and Compressor Seals
- Process Drains
- Blending Operations
- Cooling Towers
- Intermediate Storage Tanks*
- Blind Changing
- Maintenance Turnarounds (When Vessels are Vented to the Atmosphere)
- Wastewater Systems
- Barometric Condensers on Vacuum Jets
- Loading Operations*
- Sampling
- Decoking Operations*

*Not within the scope of this work.

Hydrocarbon emission sources other than stacks or vents were considered to be fugitive sources. Stacks or vents which can be identified as the principal hydrocarbon emission points were considered to be process sources. Some of the emission sources can qualify as either (or both).

Process emissions have received a great deal of study. Control technology development has been concentrated on the reduction of the emissions of hydrocarbons (and other criteria pollutants) from these sources.

Fugitive emissions, however, have received only intermittant study since 1958. Fugitive emissions sources allow hydrocarbons to escape to the atmosphere principally by accident, inadequate maintenance, or poor planning. Some hydrocarbon leakage normally occurs even in the absence of such conditions. The sources are diverse both in their physical characteristics and in the means by which they allow hydrocarbon escape.

The next step is to define the procedures by which individual fugitive sources are to be selected for sampling. Criteria were selected for choosing the refineries to be visited and units to be sampled.

Choice of Refineries and Process Units

The first step in designating specific sources for sampling was the choice of refineries. A rigorously accurate sampling procedure would include most, if not all, of the 256 refineries operating in the U.S. Such a large sampling plan would be virtually unmanageable as well as being cost-prohibitive. Therefore, a number of representative refineries were selected for sampling.

The criteria for refinery selection were age, size and location.

Age was a particularly difficult variable to utilize. After a consideration of the complexities introduced by using either the age of the entire refinery, the age of individual process units or the age of individual fittings, the choice was arbitrarily made to examine refineries newer than 10 years and older than 20 years (new and old respectively).

Size was used as a selection criteria in the anticipation that it would have an effect on the number and type of products manufactured, the number and type of hazardous species formed, the types of units available for sampling, the amount of effort put into maintenance programs, and the quality of equipment purchased. An arbitrary decision was made to use 8,000 m^3/day as the dividing line. There are 56 refineries processing more than 8,000 m^3/day of crude and 200 refineries of less capacity.

The effect of location is primarily one of availability of different crude oils and consequently the opportunity to form a different slate of potentially hazardous compounds.

The final choice of refineries was thus to be four in each geographical area of the country, i.e., East Coast, West Coast, Gulf Coast and Mid-Continent. Each set of four would be comprised of one new/large, one old/small and two old/large.

Process Units to be Sampled

Temperature and pressure were thought to have major effects upon fugitive emissions from a refinery. They are, at least, available and useful variables and are currently treated as choice parameters. In a refinery, there can be found as many combinations of temperature and pressure as one wishes to define. For the purposes of this sampling plan, four pressure/temperature classifications were employed:

- high pressure/high temperature,
- low pressure/high temperature,
- high pressure/low temperature, and
- low pressure/low temperature.

These terms are defined as follows:

- pressure -
  - . high - >1000 kPa,
  - . low - <1000 kPa, and
- temperature -
  - . high - >100°C, and
  - . low - <100°C.

Several process units fall within each category of pressure/temperature. A single unit rarely has each size, type and service that has been defined for each piece of hardware. In most cases, several units must be sampled to completely fill the required variable categories. In the event that all of the desired equipment categories do exist on one process unit, samples are still taken from as many other units as possible. This serves two purposes. Bias toward a particular unit is elimінted, generating data more representative of the pressure/temperature class as a whole. Also, differences between various units can be noted when the data are analyzed. There may not be enough data to draw firm conclusions about characteristic process emissions, but it will give indications of the factors that may be significant.

It should be noted that the four pressure/temperature classifications are simply guidelines by which units most likely to have hardware in service at the desired conditions can be identified for sampling. High pressure and temperature units also employ valves, fittings, etc. that fall into the lower pressure and temperature ranges. These are not ignored, but are also sampled to fill appropriate choice variable categories.

Statistical Approach

The Value of a Statistical Approach

Seven variables have been selected as potentially important for describing the leakage of baggable devices in refineries. The variables include device type and size, temperature and pressure of operation, gas or liquid service, and refinery location, size and age. Even after dividing the range of each variable into a minimal number of subcategories, about 8,000 samples would be required to measure the leakage from each combination of the variables just once. Obtaining a statistically significant sampling for each combination of the variables would require several times as many measurements.

Fortunately, sampling plans utilizing fewer measurements can be used to determine leakage rates within the desired accuracies. By assuming that complicated interactions between the variables are unimportant, the number of necessary measurements is reduced considerably. Factorial experimental design procedures are used to select test combinations of the variables so that the effect of each variable on the leakage rate can be determined. Analysis of variance is used to determine which variables significantly affect the leakage rate. In our case, both the magnitude of leakage rates and confidence intervals for the estimates are calculated. When appropriate, regression analysis will be used to estimate trends. Tests of the validity of the assumption that higher order interactions are negligible will indicate areas where more measurements are required.

The value of statistical experimental design is that it provides a systematic and orderly procedure for selecting a specific set of measurements for a sampling program. The design is based on assumption about the probability distributions of errors, independence of effects of different variables, and the insignificance of multivariable interactions. As the data begin to come in, the validity of our assumptions will be tested and adjustments made to the sampling plan.

Structured flexibility forms the tone of the sampling plan. The structure assures that all preconcerned measurement and analysis requirements are efficiently covered. Flexibility is maintained within a procedural framework to apply what is learned toward subsequent sampling and analysis.

Factorial Experiment Design

Standard statistical techniques have been developed for handling large numbers of variables, or "factors". The methods are especially useful when only a few values of each variable need to be considered. Some important properties of the factorial design for this program are described below.

First, a list of the variables (factors) which were expected to most strongly influence the dependent variable was prepared. In this case, the dependent variable was the leakage rate for each type of equipment. A number of levels, or ranges of values, were selected for each factor. The decision was based on a trade-off between precision of results (many levels) and economy (few levels per variable). The preliminary selections for independent variables and their numbers of levels were:

Choice of Refinery
1. four geographical locations
2. three age/size categories:
   - . new/big
   - . old/little
   - . old/big

Operating Conditions
3. four temperature/pressure combinations
4. two types of service (gas/liquid)
5. three sizes

Device Types
6. eight device types:
   - . in-line block valves
   - . in-line control valves
   - . open-end valves
   - . flanges
   - . pressure-relief devices
   - . pump seals
   - . compressor seals
   - . unit drains

Each sample was identified by a set of levels, one for each factor. For example, a measurement could be obtained for the third location, largest size, old category, second temperature/pressure category, etc.

Factorial experiment design is a systematic procedure for selecting a balanced set of experiments. All levels for each variable are tested an equal number of times, with evenly distributed values for the other variables. The result is maximum efficiency and the same data set is equally suitable for determining the effect of all factors.

Fractional replication refers to balanced subsets of the complete design which can be analyzed for the effect of each variable. The ability to analyze for higher order interactions between the variables is lost. In this program, fractional replications are used to obtain an overview of the results after a limited number of samples have been obtained. An estimate of the effect of each factor on the leakage rate is available, however, the accuracy of the estimates may still be low because of the small number of samples.

Radian felt that a sampling plan which adapted according to the early results would be the most efficient. The proposed procedure covers all possibilities by first performing a fractional replication and analyzing for the effects of all factors on the leakage rate. At this point, some types of devices or variables will be found to be adequately characterized. This could be because their contribution to total emitted hydrocarbons has been found to be small, or possibly because some factor has a small effect on the amount of emissions.

Subsequent sampling plans incorporate early data and are designed to focus on those remaining factors which are most important for understanding the total hydrocarbon emissions situation for a "typical" process unit. The order of experiments is selected so that fractional replications of variable sets will be completed at regular intervals. The results are analyzed at these times. Currently the sampling program has reached a decision point, and is in the process of undergoing a sampling plan modification so that the project goal of identifying the emission properties of equipment types and typical process units is most efficiently and thoroughly accomplished.

Number of Required Samples

As discussed above, the experimental design procedure which most efficiently utilizes the data is adaptive in nature. Therefore, before sampling begins, the number of samples necessary to achieve a given hydrocarbon emissions accuracy cannot be precisely determined. The procedures for selecting samples and analyzing the results will now be described.

The device-type variables for baggable sources are:

- 48 in-line valve categories -
  - . two gas/liquid,
  - . two block/control,
  - . three sizes,
  - . four temperature/pressure conditions,
- two open-end valve categories -
  - . sampling/drain,
- 16 flange categories -
  - . two gas/liquid,
  - . two sizes,
  - . four temperature/pressure,
- six pressure-relief device categories -
  - . two gas/liquid
  - . three temperature/pressure (low temperature/low pressure excluded),
- 99 pump-seal categories -
  - . three sizes

- four temperature/pressure,
- three shaft and packing classes,
- three Reid vapor-pressure classes (for three temperature/pressure classes),
- two Reid vapor-pressure classes (for the other temperature/pressure class),
- two unit drain types, and
- compressor seals (all compressors will be sampled).

The sampling plan for each of the first four refineries is listed below.

TABLE 2. SAMPLING PLAN

Device Type	No. of Replications	Samples Per Replication	Total Samples
In-Line Valves	4	48	192
Open-End Valves	4	2	8
Flanges	2	16	32
Pressure-Relief Devices	8	6	48
Pump Seals	1*	189	189
Unit Drains	4	2	8
Compressor Seals	1	(all)	(all)
Total Samples			477 + (all compressors)

*The replications for pump seals have been selected according to the RVP category of the fluid being pumped. Thus:

- one relicate - RVP<1.5
- two replicates - 1.5<RVP<26
- three replicates - RVP>26

The number of replications per device type is selected according to expected leakage rates and measurement accuracies.

For subsequent refineries, approximately the same number of measurements will be obtained. The distribution of samples among the device types at each stage will depend on what has been learned about:

- leakage rate for each device type,
- precision and accuracy of measurements,
- prevalence of device types in refineries (this relates leakage to total emissions), and
- relative toxicity of leakages.

The total number of baggable source samples obtained will be about 8,000 (500 each for 16 refineries).

To date, we have obtained enough data to begin to predict the precision and accuracy of many of the measurements. This alone has given sufficient basis for modifying the sampling plan. We are obtaining leakage rate estimates which are also changing the focus of the program. For example, we can establish an average leak rate for valves and compressors but the confidence interval for the compressors is an order of magnitude larger for the compressor number and this is primarily due to the small data set for compressors. If equivalent confidence intervals are desired, more compressors will have to be sampled.

Selection and Screening

The process units to be studied at any given refinery are chosen such that each unit will be studied several times during the program with more frequently used processes being studied more often than rarely-found or outdated processes. Generally, eight process units are chosen at each refinery (when a sufficient number exists). The number of fittings to be screened is then divided equally among the chosen units.

The specific fittings to be screened are then chosen from the Piping and Instrumentation Diagrams (P&ID's). The fittings are chosen so as to fit the device-type variables required by the experimental design. Only after all fittings from a given unit have been selected, does the "screener" physically enter the process unit. The fittings are screened with a hydrocarbon sniffer with a sensitivity in the ppm range.

The "screener" takes hydrocarbon level readings at four equidistant points on the circumference of the fitting in question. If any of the points gives a reading of 200 ppm hydrocarbon or greater, the fitting is tagged for sampling. The 200 ppm level corresponds approximately to a leak rate of 150 ml/hr of hexane vapor. This cut-off was arbitrarily chosen but it is approximately 10^{-3} lb/hr of hydrocarbon which would constitute a small fraction of the average leak found in the 1958 California study.

All the selected fittings are screened, provided they still exit (P&ID's can be very much out of date). All fittings leaking at a rate above the cut-off point are sampled regardless of their location. Only in rare cases is a sampling point considered inaccessible. Points as high as 50 meters have been successfully sampled as well as fittings over 300°C and 1.7 meters in diameter.

The point of screening is at the point of entry of a valve or pump shaft into the packing or seal; for flanges the entire circumference is "sniffed"; for drains the sniffer probe is held just above the rim and at every two inches on the circumference of the drain opening; and, for relief fittings, the sniffer probe is held just inside the horn or against the valve seat (depending upon design).

The "screener" records as much information about each fitting as he can obtain. This includes exact size, temperature, pressure, make and model, function, type of hydrocarbon service, etc. He then attempts to learn from the refinery personnel as much as he can about the nature of packings, frequency of maintenance, type of maintenance, age of fitting and of the packing or seal.

Within eight hours of the time that a fitting is sampled, it is rescreened. At that time, the screener obtains a second set of readings taken at the surface and at a distance of 5 cm from the surface. To date neither method of screening has shown itself to be superior in being correlated to the subsequently measured leak rate. The surface contact method, however, is at least an order of magnitude more sensitive than the other approach.

Radian is confident that usable correlation factors will result from both screening approaches. The importance of obtaining a high correlation cannot be overstated because of the necessity of finding an economical method of estimating the total amount of fugitive hydrocarbon. The use of a portable hydrocarbon sniffer may be compared, in this case, to a Level I approach.

Data from this program will begin to be available in April or May of 1978 and the final data should be released about April or May 1979.

Acknowledgements

This work is being supported by the U. S. EPA under Contract Numbers 68-02-2147, Exhibit B and 68-02-2665. The contributions of Mr. C. E. Riese and the Radian staff are gratefully acknowledged.

TOXICITY OF SECONDARY EFFLUENTS FROM TEXTILE PLANTS

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Abstract

The purpose of this study was to provide chemical and toxicological baseline data on wastewater samples collected from 32 textile plants in the United States. Raw waste and secondary effluent wastewater samples were analyzed for 129 consent decree priority pollutants, effluent guidelines criteria pollutants, and nutrients; Level 1 chemical analyses were also performed. Secondary effluent samples from the 23 plants were submitted for the following bioassays: mutagenicity, cytotoxicity, clonal assay, freshwater ecology series (fathead minnows, *Daphnia*, and algae), marine ecology series (sheepshead minnows, grass shrimp, and algae), 14-day rat acute toxicity, and soil microcosm. Based on the bioassay results, 10 of the 23 textile plants were found to have secondary effluents sufficiently toxic to proceed to a second phase of the study. In the second phase, samples will be collected from these 10 plants to determine the level of toxicity removal attained by selected tertiary treatment technologies.

Scope of Work

Background

To understand the nature and purpose of the textile wastewater toxics program it is first necessary to briefly review the events which formed the study's foundation. The principal event occurred on 1 October 1974 when the American Textile Manufacturers Institute (ATMI) filed a petition with the U.S. Fourth Circuit Court of Appeals asking for review of the 1983 effluent guidelines proposed for the textile industry. ATMI's grounds for the suit were that the best available technology economically achievable (BATEA) had not been demonstrated for the textile industry. As a result, ATMI and EPA filed a joint motion for delay of the petition, stating that additional information would be developed through a cooperative study by ATMI and EPA (IERL/RTP).

The objective of this ATMI/EPA Grant Study was to gather enough technical and economic data to determine what is the BATEA for removing criteria pollutants from textile wastewaters. Criteria pollutants for the textile industry include 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), color, sulfide, pH, chromium, phenol, and total suspended solids (TSS). On 3 January 1975 the court instructed ATMI and EPA to proceed as promptly as feasible to a completion and review of the study.

The ATMI/EPA Grant Study was divided into two phases: Phase I, to determine the best available technology, and Phase II, to determine which technology(s) was economically achievable. A generalized program outline of Phase I is shown in Figure 1. To evaluate the best available technology, two mobile pilot plants were constructed by ATMI. This strategy allowed for real-time, flowthrough treatment studies. Each pilot plant contained six tertiary wastewater treatment unit operations; one was scheduled to visit 12 textile plants and the other to visit 11.

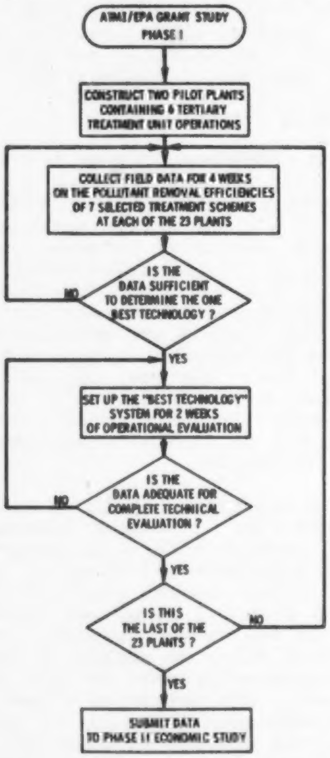
ATMI/EPA GRANT STUDY
PHASE I
CONSTRUCT TWO PILOT PLANTS CONTAINING 6 TERTIARY TREATMENT UNIT OPERATIONS
COLLECT FIELD DATA FOR 4 WEEKS ON THE POLLUTANT REMOVAL EFFICIENCIES OF 7 SELECTED TREATMENT SCHEMES AT EACH OF THE 23 PLANTS
IS THE DATA SUFFICIENT TO DETERMINE THE ONE BEST TECHNOLOGY ?
NO
YES
SET UP THE "BEST TECHNOLOGY" SYSTEM FOR 2 WEEKS OF OPERATIONAL EVALUATION
IS THE DATA ADEQUATE FOR COMPLETE TECHNICAL EVALUATION ?
NO
YES
IS THIS THE LAST OF THE 23 PLANTS ?
NO
YES
SUBMIT DATA TO PHASE II ECONOMIC STUDY

Figure 1. Program outline for Phase I: technology assessment for the ATMI/EPA Grant Study.

Treatment operations in each mobile unit include a reactor/clarifier (using combinations of alum, lime, ferric chloride, and anionic and cationic polyelectrolytes), two multimedia filters, three granular activated carbon columns, dissolved air flotation, and ozonation. Powdered activated carbon treatability tests were performed in the laboratory instead of in the field with the pilot plant. Using these six unit operations ATMI and EPA selected seven treatment systems for evaluation (Figure 2).

MODE A: REACTOR / CLARIFIER → MULTIMEDIA FILTER
MODE B: MULTIMEDIA FILTER → GRANULAR ACTIVATED CARBON COLUMNS
MODE C: MULTIMEDIA FILTER → OZONATOR
MODE D: OZONATOR
MODE E: (OPTIONAL) REACTOR / CLARIFIER → MULTIMEDIA FILTER → GRANULAR ACTIVATED CARBON → OZONATOR
MODE F: COAGULATION → MULTIMEDIA FILTER
MODE G: DISSOLVED AIR FLOTATION

Figure 2. Seven tertiary treatment modes for "best available technology" evaluation.

TABLE 1. CHEMICAL COMPOUNDS AS LISTED IN THE CONSENT DECREE

Acenaphthene
Acrolein
Acrylonitrile
Aldrin/Dieldrin
Antimony and compounds
Arsenic and compounds
Asbestos
Benzene
Benzidine
Beryllium and compounds
Cadmium and compounds
Carbon tetrachloride
Chlordane (technical mixture and metabolites)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)
Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
Chlorinated naphthalene
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
Chloroform
2-Chlorophenol
Chromium and compounds
Copper and compounds
Cyanides
DDT and metabolites
Dichlorobenzenes (1,2-,1,3-, and 1,4-dichlorobenzenes)
Dichlorobenzidine
Polychlorinated biphenyls (PCB)
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)
Selenium and compounds
Silver and compounds
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)
Tetrachloroethylene
Thallium and compounds
Toluene
Toxaphene
Trichloroethylene
Vinyl chloride
Zinc and compounds

Each of the seven systems was to be set up, and operational and pollutant data were to be collected over a 2-day to 3-day period. Based on that data, the "best" system was to be selected and set up for 2 weeks of operational evaluation. These data were then to be forwarded to Phase II for economic evaluation.

The second event that formed the foundation for this project occurred when a group of environmental action organizations filed a class action suit against EPA (Natural Resources Defense Council et al. *v.* Train, U.S. District Court of Washington, D.C.) for not developing and promulgating regulations establishing effluent limitations and guidelines and new source performance standards for 21 industrial point sources, including the textile industry. As a result, on 7 June 1976 the court issued a consent decree requiring EPA to enhance development of effluent standards.

The most significant result from the court mandate was that it focused federal water pollution control efforts on potentially toxic and hazardous pollutants. The original consent decree required that 38 classes of chemical compounds (Table 1) be analyzed in wastewater samples. Recognizing the difficulty of analyzing for all chemical species present in each category of compounds, EPA developed a list of 129 specific compounds (Appendix A) representative of the classes of compounds listed in the consent decree. These compounds are referred to as the consent decree priority pollutants, or priority pollutants for short.

EPA also developed a sampling and analytical procedures manual to be used as a laboratory guide for the analysis of priority pollutants (1). The analytical methods recommended by EPA are still in the developmental phase and require further verification and validation.

Therefore, in addition to evaluating the removal of criteria pollutants by tertiary treatment technologies, EPA was charged with the task of evaluating the removals of toxicity and priority pollutants by the treatment systems.

The final event which influenced the formation of the present program was the three-phase sampling and analytical strategy for environmental assessment developed by EPA, Process Measurements Branch, IERL/RTP. The purpose of the assessment procedure was to determine in a stepwise and cost-effective manner all chemical species being discharged to the environment from a point source. Level 1, the first part of the three-phase approach, is designed to focus available resources on emissions that have a high potential for causing measurable health or ecological effects.

The second phase, Level 2, has as its goal the identification and quantification of specific compounds. Level 3 is designed to continuously monitor indicator compounds as surrogates for a large number of specific pollutants. At the start of this textile project, only Level 1 analytical and biological procedures were available(2).

In addition to chemical analyses, the Level 1 recommended protocol included bioassay testing procedures for evaluating toxicity removal by control technologies ([3]). Bioassays are required to provide direct evidence of complex biological effects such as synergism, antagonism, and bioavailability.

Program Objective

The fundamental objective of the textile wastewaters program conducted by MRC in conjunction with the EPA is to determine the reduction in toxicity and priority pollutant concentrations achieved by the tertiary treatment technologies under investigation in the ATMI/EPA Grant Study. The latter study focuses directly on the treatability of criteria pollutants. Thus the overall textile program consists of two separate projects, each with different activities, running parallel in time, but converging towards the same goal: determination of the best available technology economically achievable for removing pollutants from textile wastewaters (Figure 3).

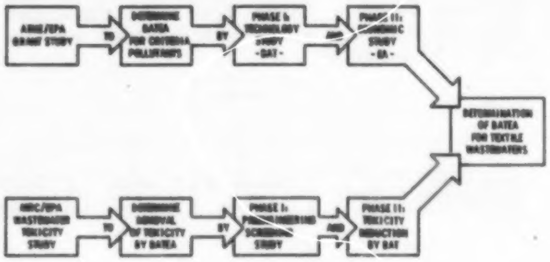
ATMI/EPA GRANT STUDY
TO
DETERMINE BATEA FOR CRITERIA POLLUTANTS
BY
PHASE I: TECHNOLOGY STUDY -BAT-
AND
PHASE II: ECONOMIC STUDY -EA-
MRC/EPA WASTEWATER TOXICITY STUDY
TO
DETERMINE REMOVAL OF TOXICITY BY BATEA
BY
PHASE I: PREENGINEERING SCREENING STUDY
AND
PHASE II: TOXICITY REDUCTION BY BAT
DETERMINATION OF BATEA FOR TEXTILE WASTEWATERS

Figure 3. Overall program approach to determine BATEA.

To evaluate the reduction in toxicity in a cost-effective manner for the MRC/EPA project, a two-phase approach was developed. Phase I was designed to collect baseline toxicity data on secondary effluents from 23 selected textile plants and to rank the plants in descending order of toxicity (Figure 4). Phase II was designed to determine the level of toxicity removal attained by the tertiary treatment systems in the ATMI/EPA Grant Study at only those plants with relatively high secondary effluent toxicity (Figure 5). Sampling locations for Phase II of the study are shown in Figure 6, and the strategy used for evaluating control technologies in terms of toxicity removal is illustrated in Figure 7.

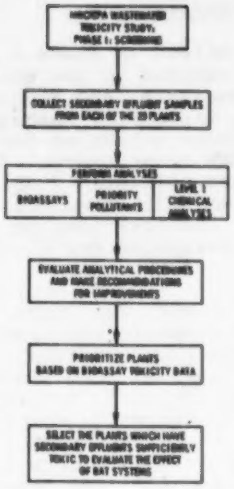
MRC/EPA WASTEWATER TOXICITY STUDY: PHASE I: SCREENING
COLLECT SECONDARY EFFLUENT SAMPLES FROM EACH OF THE 23 PLANTS
PERFORM ANALYSES
BIOASSAYS
PRIORITY POLLUTANTS
LEVEL 1 CHEMICAL ANALYSES
EVALUATE ANALYTICAL PROCEDURES AND MAKE RECOMMENDATIONS FOR IMPROVEMENTS
PRIORITIZE PLANTS BASED ON BIOASSAY TOXICITY DATA
SELECT THE PLANTS WHICH HAVE SECONDARY EFFLUENTS SUFFICIENTLY TOXIC TO EVALUATE THE EFFECT OF BAT SYSTEMS

Figure 4. Program outlined for Phase I of the MRC/EPA wastewater toxicity study.

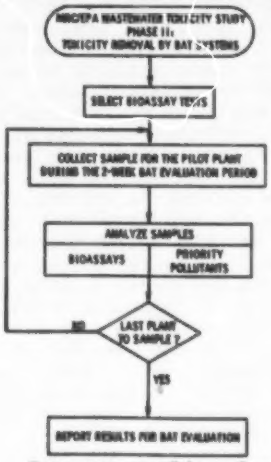
MRC/EPA WASTEWATER TOXICITY STUDY PHASE II: TOXICITY REMOVAL BY BAT SYSTEMS
SELECT BIOASSAY TESTS
COLLECT SAMPLE FOR THE PILOT PLANT DURING THE 2-WEEK BAT EVALUATION PERIOD
ANALYZE SAMPLES
BIOASSAYS
PRIORITY POLLUTANTS
LAST PLANT TO SAMPLE ?
NO
YES
REPORT RESULTS FOR BAT EVALUATION

Figure 5. Program outline for Phase II of the MRC/EPA wastewater toxicity study.

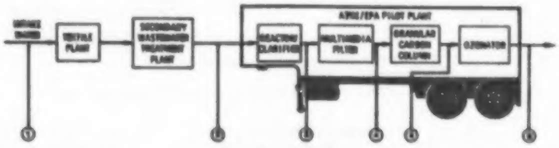
INTAKE WATER
TEXTILE PLANT
SECONDARY WASTEWATER TREATMENT PLANT
ATMI/EPA PILOT PLANT
REACTOR/CLARIFIER
MULTIMEDIA FILTER
GRANULAR CARBON COLUMN
OZONATOR

Figure 6. Sampling locations for Phase II of the MRC/EPA wastewater toxicity study.

BIOASSAY RESULTS		TOXIC SUBSTANCE INTERPRETATION
INLET	OUTLET	
+	+	CONTROL TECHNOLOGY IS NOT EFFECTIVE
+	-	CONTROL TECHNOLOGY IS EFFECTIVE
-	+	CONTROL TECHNOLOGY IS DETRIMENTAL
-	-	CONTROL TECHNOLOGY IS NOT DETRIMENTAL

Figure 7. Interpretation of bioassay test results.

Project Organization

The major effort in Phase I of the MRC/EPA study was devoted to the collection, chemical analysis, and biological toxicity testing of wastewater samples from the 23 textile plants scheduled for testing in the ATMI/EPA Grant Study. In addition, samples were collected from nine other textile plants for chemical analyses only. Wastewater characterization data were therefore assembled for a total of 32 plants.

The scope of work for Phase I was divided into three separate task areas, each based on different EPA data requirements, as shown in Figure 8. CPB (Chemical Processes Branch, IERL/RTP, Project Officer, M. Samfield) requested chemical and bioassay data on secondary effluent samples from the 23 textile plants scheduled to be studied in the ATMI/EPA Grant Study. These data were used to characterize and compare the relative toxicities of the plant effluents tested. EGD (Effluent Guidelines Division, EPA, Washington, D.C., J. D. Gallup) requested chemical analyses of the raw waste streams entering the 23 wastewater treatment plants, as well as chemical analyses of the raw waste and secondary effluent streams at 9 additional textile plants. Raw waste and effluent data were needed to evaluate the pollutant removal efficiencies of current state-of-the-art secondary treatment systems. In order to implement the entire Level 1 Environmental Assessment Protocol, PMB (Process Measurements Branch, IERL/RTP, L. D. Johnson) requested that Level 1 chemical characterization also be performed on the effluent samples at the basic 23 textile plants (2). Since these data were requested after the program began, only 15 textile plants were sampled for Level 1 chemical characterization.

Chemical characterization of wastewater samples involves four categories of analysis:

- 129 consent decree priority pollutants analysis (1)
- nutrient analysis (4, 5)
- effluent guidelines criteria pollutants analysis (4, 5)
- Level 1 chemical characterization (2)

The 129 consent decree priority pollutants as listed in Appendix A are divided into volatile compounds, nonvolatile compounds, and metals. The nutrient series required to support algal tests includes analysis of nitrite, nitrate, ammonia, total Kjeldahl nitrogen (TKN), *o*-phosphate, phosphorus, and total organic carbon (TOC). Effluent guidelines criteria pollutants include 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), sulfide, color, pH, total suspended solids (TSS), total dissolved solids (TDS), and total phenol.

The bioassay scheme established by EPA for evaluating the reduction in toxicity of water samples is shown in Figure 9. All the tests shown were used in this project. The marine ecology series and the soil microcosm tests were requested after the project began. These data were obtained from 15 textile plants as opposed to the basic 23 plants.

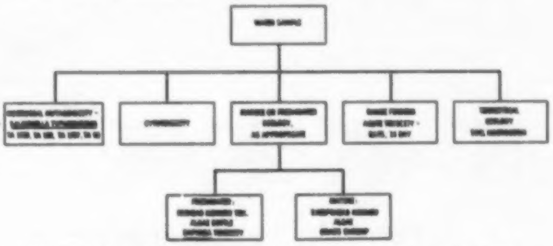

Figure 9. EPA-recommended bioassay testing scheme for toxicity analysis of water samples.

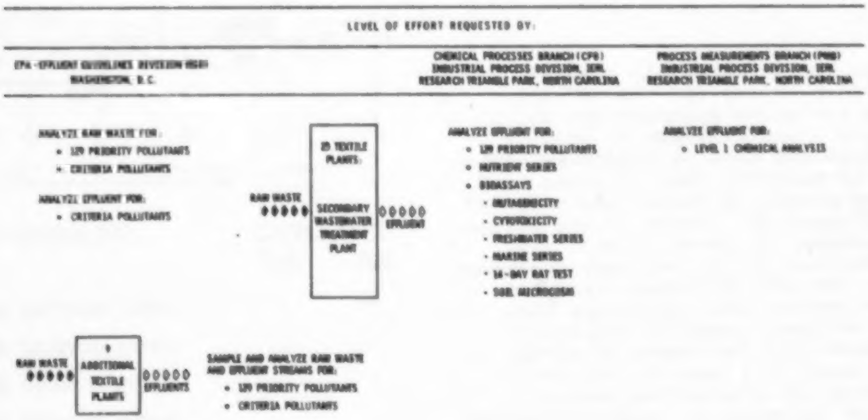
LEVEL OF EFFORT REQUESTED BY:
EPA-EFFLUENT GUIDELINES DIVISION (EGD) WASHINGTON, D.C.
CHEMICAL PROCESSES BRANCH (CPB) INDUSTRIAL PROCESS DIVISION, IERL RESEARCH TRIANGLE PARK, NORTH CAROLINA
PROCESS MEASUREMENTS BRANCH (PMB) INDUSTRIAL PROCESS DIVISION, IERL RESEARCH TRIANGLE PARK, NORTH CAROLINA
ANALYZE RAW WASTE FOR:
• 129 PRIORITY POLLUTANTS
• CRITERIA POLLUTANTS
ANALYZE EFFLUENT FOR:
• CRITERIA POLLUTANTS
RAW WASTE
23 TEXTILE PLANTS:
SECONDARY WASTEWATER TREATMENT PLANT
EFFLUENT
ANALYZE EFFLUENT FOR:
• 129 PRIORITY POLLUTANTS
• NUTRIENT SERIES
• BIOASSAYS
• MUTAGENICITY
• CYTOTOXICITY
• FRESHWATER SERIES
• MARINE SERIES
• 14-DAY RAT TEST
• SOIL MICROCOSM
ANALYZE EFFLUENT FOR:
• LEVEL 1 CHEMICAL ANALYSIS
RAW WASTE
9 ADDITIONAL TEXTILE PLANTS
EFFLUENTS
SAMPLE AND ANALYZE RAW WASTE AND EFFLUENT STREAMS FOR:
• 129 PRIORITY POLLUTANTS
• CRITERIA POLLUTANTS

Figure 8. Scope of work for the analysis of textile plant wastewaters.

Figure 10 illustrates the distribution of samples among the eight EPA and private laboratories that performed the chemical analyses and bioassay tests.

MRC collected raw wastes and effluent samples at 23 of the ATMI/EPA-designated plants. Wastewater samples were collected by EPA-Environmental Research Laboratory (ERL) (Athens, Georgia) at two of the additional textile plants and sent to MRC for chemical analysis. Sverdrup and Parcel and Associates, Inc., (St. Louis, Missouri) collected the remaining samples at the additional seven plants and sent them to MRC for chemical analysis.

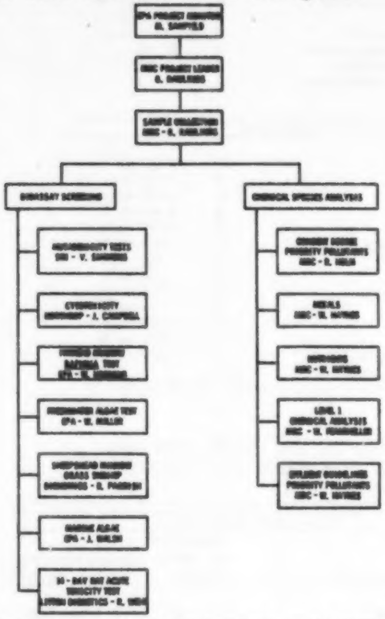

Figure 10. Laboratories and persons involved in sample analysis of textile plant effluents.

Grab samples and 8-hr continuous samples were collected both before and after the wastewater treatment system at each of the 32 plants (Figure 11). Samples were stored in ice at 4°C and shipped by air freight to the laboratories for analysis. Chemical analyses and bioassays were performed at eight EPA and commercial laboratories.

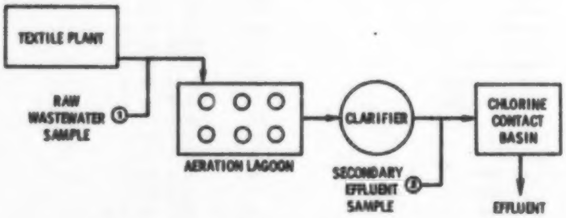

Figure 11. Phase I sampling locations.

Summary of Results

Chemical Analyses

Analysis for the 129 priority pollutants in raw waste and secondary effluent samples (totaling 64 samples) was performed by Monsanto Research Corporation (MRC). Analytical procedures followed those recommended by EPA. However, the recommended analytical protocol for priority pollutant analysis is still in the developmental stage and requires further verification and validation. Consequently, the analytical results of textile wastewater samples must be looked upon as good estimates of which priority pollutants are present, with concentrations accurate to within ±100%.

The 129 priority pollutants were divided into 5 fractions for analysis: volatile compounds, base/neutral compounds, acid compounds, pesticides and polychlorinated biphenyls (PCB), and metals. The EPA protocol recommended that laboratories not acquire analytical standards for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) because of its extreme toxicity (^{1}). Asbestos was omitted due to the presence of other fibrous materials in textile wastewaters.

A summary of the organic compounds found in the 32 raw waste and 32 secondary effluent samples is given in Tables 2 and 3. Of the 114 organic compounds on the priority pollutant list, a total of 56 different compounds were found, 49 in raw waste samples and 46 in secondary effluent samples. The number of compounds found at each plant is summarized in Table 4. On an individual plant basis the greatest number of organic compounds found in a raw waste and in a secondary effluent sample were 20 and 14, respectively, with an average number per plant of 11 in the raw waste and 9 in the secondary effluent. The predominant compounds were bis(2-ethylhexyl) phthalate in 57 samples (0.5 mg/m^3 to 300 mg/m^3), toluene in 46 samples (0.4 mg/m^3 to 1,400 mg/m^3), and α-hexachlorocyclohexane (α-BHC) in 43 samples (0.02 mg/m^3 to 6 mg/m^3).

Note that pesticides were not analyzed in raw waste and secondary effluent samples from the last seven plants listed in Table 5. Also, plant R was inadvertently sampled between the aeration lagoon and settling pond and is not a typical secondary effluent sample.

The frequency of occurrence of 56 organic species in 64 wastewater samples is given in Table 5. Dominant compounds were bis(2-ethylhexyl) phthalate found in 56 samples, toluene found in 46 samples, and α-hexachlorocyclohexane (α-BHC) found in 43 samples.

A summary of the 13 priority pollutant metals and cyanide concentrations in raw waste and secondary effluent samples is

TABLE 2. SUMMARY OF PRIORITY POLLUTANTS FOUND IN RAW WASTE SAMPLES, FROM 129 TOTAL, SHOWING CONCENTRATION RANGES AND NUMBER OF PLANTS WHERE THE SPECIES WERE IDENTIFIED

Volatile organic			Base/neutral organic		
Compound	Number of times found	Concentration range, mg/m^3	Compound	Number of times found	Concentration range, mg/m^3
Toluene	22	2 to 300	Naphthalene	18	0.03 to 300
Benzene	4	5 to 200	Dimethyl phthalate	5	3 to 110
Chloroform	12	2 to 500	Diethyl phthalate	12	0.2 to 70
Chlorobenzene	6	1 to 300	Bis(2-ethylhexyl) phthalate	27	0.5 to 300
Ethylbenzene	20	0.7 to 2,800	1,4-Dichlorobenzene	5	1 to 210
Trichlorofluoromethane	2	30 to 50	1,2,4-Trichlorobenzene	8	30 to 440
1,1,1-Trichloroethane	6	2 to 300	1,2-Dichlorobenzene	8	0.1 to 300
Trichloroethylene	7	2 to 200	Anthracene	1	0.1
1,1,2,2-Tetrachloroethylene	8	6 to 2,100	Pyrene	1	0.9
Trans-1,2,-dichloroethylene	1	2	Acenaphthene	7	9 to 270
1,1-Dichloroethane	2	0.6 to 4	Di-n-butyl phthalate	6	2 to 60
1,2-Dichloropropane	1	2	Fluorene	2	5 to 15
Cis-1,3-dichloropropene	1	2	Hexachlorobenzene	2	0.5 to 2
			N-Nitrosodiphenylamine	1	11
			2,6-Dinitrotoluene	1	50
			Indeno(1,2,3-cd)pyrene	1	2
Acid organic			**Pesticide**		
Phenol	19	0.5 to 100	α-BHC	17	0.02 to 6
Pentachlorophenol	8	2 to 70	β-BHC	8	0.03 to 2
2-Nitrophenol	1	70	γ-BHC	11	0.03 to 4
p-Chloro-*m*-cresol	2	5 to 8	δ-BHC	8	0.07 to 2
4-Nitrophenol	1	70	Heptachlor	7	0.03 to 6
2,4,6-Trichlorophenol	2	0.7 to 20	α-Endosulfan	11	0.1 to 8
2-Chlorophenol	1	130	β-Endosulfan	7	0.1 to 4
			Aldrin	9	0.1 to 3
			Dieldrin	14	0.2 to 6
			Endrin	6	1 to 3
			4,4'-DDT	2	0.07 to 0.2
			4,4'-DDD	7	0.1 to 2
			Heptachlor epoxide	4	0.2 to 0.4

TABLE 3. SUMMARY OF PRIORITY POLLUTANTS FOUND IN EFFLUENT SAMPLES, FROM 129 TOTAL, SHOWING CONCENTRATION RANGES AND NUMBER OF PLANTS WHERE THE SPECIES WERE IDENTIFIED

Volatile organic			Base/neutral organic		
Compound	Number of times found	Concentration range, mg/m^3	Compound	Number of times found	Concentration range, mg/m^3
Toluene	24	0.4 to 1,400	Naphthalene	6	0.5 to 250
Benzene	2	0.5 to 60	Dimethyl phthalate	3	0.2 to 1
Chloroform	5	7 to 60	Diethyl phthalate	9	0.5 to 10
Chlorobenzene	2	4 to 30	Bis(2-ethylhexyl)phthalate	30	2 to 230
Ethylbenzene	9	0.7 to 3,000	1,4-Dichlorobenzene	3	0.05 to 2
Trichlorofluoromethane	6	2 to 2,100	1,2,4-Trichlorobenzene	6	2 to 920
Trichloroethylene	2	5 to 80	1,2-Dichlorobenzene	5	0.2 to 6
1,1,2,2-Tetrachloroethylene	3	0.4 to 40	Anthracene	1	4
Cis-1,3-dichloropropene	1	6	N-Nitroso-di-n-propylamine	2	2 to 20
Trans-1,3-dichloropropene	2	0.9 to 4	Pyrene	4	0.1 to 0.3
Bromodichloromethane	1	2	Acenaphthene	2	0.5 to 2
			Di-n-butyl phthalate	3	4 to 60
			Hexachlorobenzene	3	0.3 to 0.8
			Butylbenzyl phthalate	1	70
Acid organic			**Pesticides**		
Phenol	2	2 to 3	α-BHC	26	0.07 to 6
Pentachlorophenol	1	60	β-BHC	14	0.1 to 3
2,4-Dimethylphenol	2	8 to 9	γ-BHC	18	0.1 to 2
p-chloro-*m*-cresol	1	2	δ-BHC	3	0.06 to 0.3
2,4,6-Trichlorophenol	1	20	Heptachlor	9	0.2 to 4
Chloro cresol	1	30	α-Endosulfan	18	0.04 to 2
2-Chlorophenol	1	10	β-Endosulfan	8	0.2 to 1
			Aldrin	11	0.1 to 2
			Dieldrin	14	0.2 to 1
			Endrin	5	0.2 to 1
			4,4'-DDT	9	0.1 to 2
			4,4'-DDD	3	0.2 to 1
			4,4'-DDE	4	0.1 to 0.4
			Heptachlor epoxide	2	0.3

TABLE 4. NUMBER OF PRIORITY ORGANIC POLLUTANTS FOUND IN THE RAW WASTE AND SECONDARY EFFLUENT STREAMS

	Number of organic compounds detected[a]	
Plant	In raw waste	In secondary effluent
A	11	13
B	9	8
C	15	13
D	10	9
E	20	9
F	19	12
G	12	10
H	17	8
J	10	11
K	13	12
L	12	7
M	10	9
N	15	13
P	14	10
R	14	11[b]
S	16	13
T	9	5
U	12	12
V	14	6
W	16	11
X	10	10
Y	9	12
Z	12	10
C-001	6	NA[c]
Y-001	15	8
JJ[d]	6	2
KK[d]	11	6
LL[d]	8	2
MM[d]	1	4
NN[d]	2	1
OO[d]	5	3
PP[d]	5	NA

[a] In the list of priority pollutants there are 114 organic compounds.

[b] Sample inadvertently collected prior to the settling pond.

[c] Not applicable; these plants discharge their wastewater to a municipal treatment system.

[d] Pesticides were not analyzed at this plant.

TABLE 5. OCCURRENCE OF PRIORITY ORGANIC POLLUTANTS COMBINED FROM RAW WASTE AND SECONDARY EFFLUENT SAMPLES

Priority pollutant	Number of samples in which pollutant was detected[a]			Observed concentration range,[b] mg/m^3
	Total	Raw waste samples	Secondary effluent samples	
Bis(2-ethylhexyl) phthalate	57	27	30	0.5 to 300
Toluene	46	22	24	0.4 to 1,400
α-BHC	43	17	26	0.02 to 6
γ-BHC	29	11	18	0.03 to 4
Ethylbenzene	29	20	9	0.7 to 3,000
α-Endosulfan	29	11	18	0.04 to 8
Dieldrin	28	14	14	0.2 to 6
Naphthalene	24	18	6	0.03 to 300
β-BHC	22	8	14	0.03 to 3
Diethyl phthalate	21	12	9	0.2 to 70
Phenol	21	19	2	0.5 to 100
Aldrin	20	9	11	0.1 to 3
Chloroform	17	12	5	2 to 500
Heptachlor	16	7	9	0.03 to 6
β-Endosulfan	15	7	8	0.1 to 4
1,2,4-Trichlorobenzene	14	8	6	2 to 900
1,2-Dichlorobenzene	13	8	5	0.1 to 300
1,1,2,2-Tetrachloroethylene	11	8	3	0.4 to 2,100
Endrin	11	6	5	0.2 to 3
δ-BHC	11	8	3	0.06 to 2
4,4'-DDT	11	2	9	0.1 to 2
4,4'-DDD	10	7	3	0.1 to 2
Acenaphthene	9	7	2	0.5 to 270
Di-n-butyl phthalate	9	6	3	2 to 60
Pentachlorophenol	9	8	1	2 to 70
Trichloroethylene	9	7	2	2 to 200
Dimethyl phthalate	8	5	3	0.2 to 110
1,4-Dichlorobenzene	8	5	3	0.05 to 200
Chlorobenzene	8	6	2	1 to 300
Trichlorofluoromethane	8	2	6	2 to 2,100
Benzene	6	4	2	0.5 to 200
1,1,1-Trichloroethane	6	6	0	2 to 300
Heptachlor epoxide	6	4	2	0.2 to 0.4
Pyrene	5	1	4	0.1 to 0.9
Hexachlorobenzene	5	2	3	0.3 to 2
4,4'-DDE	4	0	4	0.1 to 0.4
p-Chloro-m-cresol	3	2	1	2 to 8
2,4,6-Trichlorophenol	3	2	1	0.7 to 20
Anthracene	2	1	1	0.1 to 4
N-nitroso-di-n-propylamine	2	0	2	2 to 20
Fluorene	2	2	0	5 to 15
1,1-Dichloroethane	2	2	0	0.6 to 4
Cis-1,3-dichloropropene	2	1	1	2 to 6
Trans-1,3-dichloropropene	2	0	2	0.9 to 4
2,4-Dimethylphenol	2	0	2	8 to 9
2-Chlorophenol	2	1	1	10 to 130
N-nitrosodiphenylamine	1	1	0	11
2,6-Dinitrotoluene	1	1	0	50
Indeno(1,2,3-cd)pyrene	1	1	0	2
Butylbenzyl phthalate	1	0	1	70
Trans-1,2-dichloroethylene	1	1	0	2
1,2-Dichloropropane	1	1	0	2
2-Nitrophenol	1	1	0	70
4-Nitrophenol	1	1	0	70
Chloro cresol	1	0	1	30
Bromodichloromethane	1	0	1	2

[a] Out of a total of 64 samples.

[b] Rounded to one significant figure.

given in Table 6, which also summarizes the criteria pollutant and nutrient concentrations for secondary effluent samples. Nutrient analyses were performed to support freshwater algae bioassays.

On an individual plant basis it was frequently observed, especially for the metals data, that the concentration of a specific pollutant was greater in the secondary effluent sample than in the raw waste sample. This phenomenon is due, in part, to the hydraulic retention time of the wastewater treatment facility. Since raw waste and secondary effluent samples were collected simultaneously, concentrations in the secondary effluent were due to raw waste loads that entered the treatment system 1 day to 30 days prior to sampling. The average retention time for the 32 plants was about 5 days.

Level 1 chemical analyses were performed on secondary effluent samples from 15 of the 23 basic textile plants. Level 1 protocol identifies classes of compounds present in environmental samples and measures the general concentration range. Results indicate that total concentration of methylene chloride extractable organics ranges from 3 g/m^3 to 64 g/m^3. This value is 5 to 10 times lower than the range for total organic carbon (Table 6).

In the Level 1 procedure each sample was fractionated by a liquid chromatography column into eight fractions based on polarity. Infrared analysis of each fraction indicated the presence of aliphatic hydrocarbons, esters and acids, aromatic compounds, phthalate esters, and fatty acid groups. Low resolution mass spectrophotometric analysis of the eight fractions of each sample detected the following types of compounds: paraffinic/olefinic, alkyl benzenes, alcoholic ethers, di-n-octyl phthalate, bis(hydroxy-t-butyl phenol) propane, tri-t-butyl benzene, alkyl phenols, dichloroaniline, toluene-sulfonyl groups, vinyl stearate and azo compounds.

Bioassay of Secondary Effluents

The primary objective of the entire wastewater toxicity study is to determine the level of toxicity removal from secondary wastewater achieved by the tertiary treatment technologies selected for the ATMI/EPA BATEA study. To this end, the purpose of this screening study was to provide chemical and toxicological baseline data on secondary effluents from the 23 textile plants and to select plants for the toxicity removal study.

Bioassays used were selected by EPA and included tests for assessment of both health and ecological effects (^{3}). Health effects tests estimated the potential mutagenicity, potential or presumptive carcinogenicity, and potential toxicity of the secondary effluent wastewater samples to mammalian organisms. Ecological effects tests focused on the potential toxicity of samples to vertebrates (fish), invertebrates (daphnids and shrimp), and plants (algae) in freshwater, marine, and terrestrial ecosystems.

Biological testing, as well as chemical and physical parameters, must be considered when assessing the potential impact of industrial or municipal/industrial wastewaters on the aquatic environment. Biological testing involves determination of toxicity for samples of treated effluents. In a toxicity test, aquatic organisms will integrate the synergistic and antagonistic effects of all the effluent components over the duration of exposure.

Although toxicity tests with aquatic organisms can be conducted by applying wastewater samples directly to the test organisms, or by injection or feeding, most tests are conducted by exposing the test organisms to test solutions containing various concentrations of effluent samples. One or more controls are used to provide a measure of test acceptability by giving some indication of test organism health and the suitability of dilution water, test conditions, handling procedures, etc. A control test is an exposure of the organisms to dilution water with no effluent sample added. Bioassay tests are exposures of test organisms to dilution water with effluent samples added. Generally the most important data obtained from a toxicity test are the percentages of test organisms that are affected in a specified way by each concentration of wastewater sample added. The result derived from these data is a measure of the toxicity of the effluent sample to the test organisms under the test conditions.

Acute toxicity tests are used to determine the level of toxic agent that produces an adverse effect on a specified percentage of test organisms in a short period of time. The most common acute toxicity test is the acute mortality test. Experimentally, 50% effect is the most reproducible measure of the toxicity of a toxic agent to a group of test organisms, and 96-hr is often a convenient, reasonably useful exposure duration. The 96-hr median lethal concentration (96-hr LC_{50}) is most often used with fish and macroinvertebrates. Thus the acute mortality test is a statistical estimate of the LC_{50}, which is the concentration of toxicant in dilution water that is lethal to 50% of the test organisms during continuous exposure for a specified period of time. However, the 48-hr median effective concentration (48-hr EC_{50}), based on immobilization, is most often used with daphnids. The terms median lethal concentration (LC_{50}) and median effective concentration (EC_{50}) are consistent with the widely used terms median lethal dose (LD_{50}) and median effective dose (ED_{50}), respectively.

TABLE 6. SUMMARY OF METAL, CRITERIA POLLUTANT, AND NUTRIENT ANALYSES

Metal			Criteria pollutant[a]		Nutrient[a]	
	Concentration range, g/m^3					
Element	Raw waste sample	Secondary effluent sample	Pollutant	Concentration range, g/m^3	Parameter	Concentration range, g/m^3
Antimony	0.0005 to 0.06	0.0005 to 0.07	BOD_5[b]	<5 to 170	Nitrite	0 to 17
Arsenic	0.005 to 0.2	0.005 to 0.02	COD[c]	45 to 1,600	Nitrate	0.002 to 40
Beryllium	<0.0001	<0.0001	Color (APHA)[d]	10 to 2,500	Ammonia	0.02 to 14
Cadmium	0.0005 to 0.05	0.0005 to 0.01	Sulfide	0.01 to 6	TKN[e]	2 to 40
Chromium	0.0002 to 0.9	0.0002 to 2.0	Phenol	0.01 to 0.2	o-Phosphate	0.02 to 11
Copper	0.0002 to 2.4	0.0002 to 0.3	TSS[f]	0.02 to 580	Total phosphorus	0.4 to 15
Cyanide	0.004 to 0.2	0.004 to 0.2	pH	5.8 to 10	TOC[g]	19 to 260
Lead	0.001 to 0.2	0.001 to 0.2				
Mercury	0.0005 to 0.004	0.0005 to 0.0009				
Nickel	0.01 to 0.2	0.01 to 0.2				
Selenium	<0.005	<0.005				
Silver	0.005 to 0.1	0.005 to 0.1				
Thallium	<0.005	<0.005				
Zinc	0.03 to 8.0	0.07 to 38				

[a] For secondary effluent samples.
[b] 5-day biochemical oxygen demand.
[c] Chemical oxygen demand.
[d] American Public Health Association color standards.
[e] Total Kjehldahl nitrogen.
[f] Total suspended solids.
[g] Total organic carbon.

"Concentration" refers to the amount of toxicant per unit volume of test solution; "dose" refers to the measured amount of toxicant given to the test organism.

A total of 8 biological systems were used for wastewater toxicity evaluation, utilizing 21 different tester organisms. Specific tests used and the purpose of each bioassay are summarized in Table 7.

TABLE 7. BIOASSAY TESTS USED TO EVALUATE THE TOXICITY OF SECONDARY EFFLUENTS

Bioassay test system	Indicator organisms	Purpose of test
Microbial mutagenicity	*Salmonella typhimurium* (Ames test) (Strains TA1535, TA1537, TA98, TA100) *Escherichia coli* (Strains WP2, W3110, p3478) *Bacillus subtilis* (Strains H17 and M45) *Saccharomyces cerevisiae* (Strain D3)	To determine if a chemical mutagen (possibly a carcinogen) is present. These microbial strains were selected because of their sensitivity to various classes of chemical compounds.
Cytotoxicity	Rabbit alveolar macrophage (RAM) (viability and ATP determinations) Chinese hamster ovary cells	To measure metabolic impairment and death in mammalian cells. These primary cell cultures have some degree of metabolic repair capability.
Freshwater static bioassay	*Pimephales promelas* (fathead minnow) *Daphnia pulex* (daphnid)	To detect potential toxicity to organisms in aquatic environments.
Freshwater algal assay	*Selenastrum capricornutum*	To detect potential toxicity to aquatic plants.
Marine static bioassay	*Cyprinodon variegatus* (sheepshead minnow) *Palaemonetes pugio* (grass shrimp)	To detect potential toxicity to organisms in a marine environment.
Marine algal assay	*Skeletonema costatum*	To detect potential toxicity to marine plants.
Range finding acute toxicity	Rats (Charles River CD strain)	To detect potential toxicity to whole animals.
Terrestrial ecology	Soil microorganisms	To determine potential effects on soil ecosystems.

Under guidance of appropriate EPA Technical Advisors, four of the eight bioassays were performed at commercial laboratories experienced with the bioassays. The remaining four bioassays were performed by the EPA Technical Advisor, as shown in Figure 12.

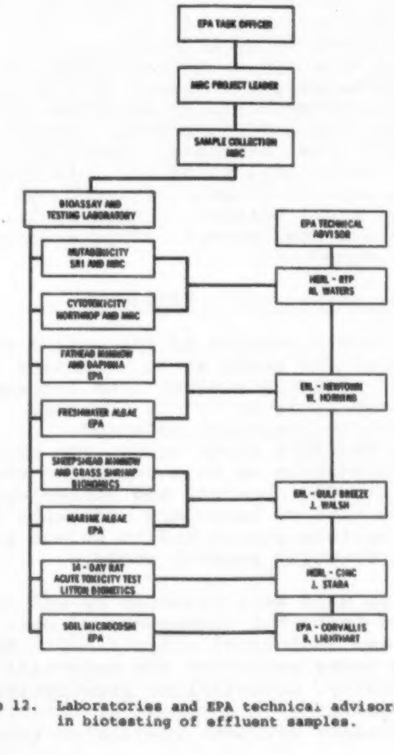
EPA TASK OFFICER
MRC PROJECT LEADER
SAMPLE COLLECTION MRC
BIOASSAY AND TESTING LABORATORY
MUTAGENICITY SRI AND MRC
CYTOTOXICITY NORTHROP AND MRC
FATHEAD MINNOW AND DAPHNIA EPA
FRESHWATER ALGAE EPA
SHEEPSHEAD MINNOW AND GRASS SHRIMP BIONOMICS
MARINE ALGAE EPA
14 - DAY RAT ACUTE TOXICITY TEST LITTON BIONETICS
SOIL MICROCOSM EPA
EPA TECHNICAL ADVISOR
HERL - RTP M. WATERS
ERL - NEWTOWN W. HORNING
ERL - GULF BREEZE J. WALSH
HERL - CINC J. STARA
EPA - CORVALLIS R. LIGHTHART

Figure 12. Laboratories and EPA technical advisors involved in biotesting of effluent samples.

A summary of the bioassay results is presented in Table 8. Toxicity is expressed as the percent of a secondary effluent solution that will cause the effect specified for each bioassay over the testing period. For the cytotoxicity, *Daphnia* and algal bioassays an Effective Concentration 20 or 50 (EC_{20} or EC_{50}) was calculated. EC_{20} for the cytotoxicity test means the concentration of secondary effluent which impairs metabolic processes in 20% of the test cells.

The viability test is a measure of the cells' ability to survive exposure to the sample, and the adenosine triphosphate (ATP) test measures the quantity of the coenzyme ATP produced, indirectly measuring cellular metabolic activity.

EC_{50} for the algal tests means the concentration of secondary effluent which causes a 50% reduction in algal growth as compared to a control sample. The freshwater algae test was performed over a 14-day period and the marine algae test over a 96-hr period.

For the fathead minnow, sheepshead minnow, and grass shrimp bioassays, death was used to measure toxicity, which was expressed as Lethal Concentration 50 (LC_{50}). LC_{50} indicates the calculated concentration of secondary effluent that is expected to cause the death of 50% of the test species. Since rats were given a specific quantity of secondary effluent, toxicity was expressed as Lethal Dose 50 (LD_{50}). LD_{50} indicates the quantity of material fed to the rats that resulted in the death of 50% of the test animals.

The measure of toxicity to a soil microcosm was the quantity of carbon dioxide (CO_2) produced after sample exposure as compared to a control sample. The quantity of CO_2 produced over a 3-wk period after subtracting the quantity produced by the control was plotted on graph paper. The slope of the curve then represented the rate of increase or decrease in CO_2 production due to addition to the sample.

Plant Ranking by Relative Wastewater Toxicity

The primary objective of the Phase I screening study was to rank textile plants according to the toxicity of their secondary wastewater and to select plants for detailed toxicity evaluation in Phase II. To accomplish this objective, members of the EPA Bioassay Subcommittee met to evaluate the bioassay data. Members of the Subcommittee are illustrated as EPA Technical Advisors in Figure 12. A summary of all the bioassay results is given in Table 7.

Data evaluation began with ranking of the plants in each set of bioassays. Results are discussed in the following sections.

Freshwater Ecology Series

Results from these tests showed sufficient variation to permit relative ranking of the toxicity of effluent samples. A composite ranking based on the responses of fathead minnows and *Daphnia* is shown in Table 9. No general rule can be made concerning the relative response between fathead minnows and *Daphnia*. For example, Plant E's effluent was significantly toxic to *Daphnia* but not toxic at all to fathead minnows; at Plant T, the reverse was true.

TABLE 8. SUMMARY OF BIOTEST DATA FOR SECONDARY EFFLUENT WASTEWATER SAMPLES[a,b]

	Cytotoxicity		Freshwater ecology series			Marine ecology series			
Plant	Viability (24-hr EC_{20}), % secondary effluent	ATP (24-hr EC_{20}), % secondary effluent	Fathead minnow (96-hr LC_{50}), % secondary effluent	Daphnia (48-hr EC_{50}), % secondary effluent	Algae[c] (14-day EC_{50}), % secondary effluent	Sheepshead minnow (96-hr LC_{50}), % secondary effluent	Grass shrimp (96-hr LC_{50}), % secondary effluent	Algae[c] (96-hr EC_{50}), % secondary effluent	Soil microcosm, normalized relative CO_2 rate change,[d]
A	NAT[e]	NAT	19.0	9.0	76	62.0	31.2	-[f]	-0.031
B	NAT	NAT	NAT	NAT	30	NAT	NAT	-[g]	0.000
C	16.8[h]	6.1[h]	46.5	41.0	0[i]	69.5	13.6	-[f]	-0.065
D	NAT	NAT	NAT	NAT	0[i]	-[f]	-[f]	-[f]	-0.099
E	NAT	NAT	NAT	7.0	2[j]	NAT	NAT	10 to 50	-0.060
F	NAT	9.4	NAT	81.7	0[i]	NAT	NAT	85	-0.039
G	NAT	NAT	64.7	62.4	0	NAT	NAT	-[f]	0.017
H	NAT	NAT	-[k]	60% dead at 100% concentration	96	-[f]	-[f]	-[f]	-0.083
J	NAT	NAT	NAT	NAT	0[i]	-[f]	-[f]	-[f]	-0.163
K	NAT	NAT	NAT	NAT	0	NAT	NAT	77	-0.094
L	NAT	4.0	22.5	28.0	42[i]	NAT	NAT	-[f]	-0.020
M	NAT	NAT	NAT	60.0	0[j]	-[f]	-[f]	-[f]	-0.058
N	13.3	3.0	40.0	100% dead at all dilutions	2	47.5	36.3	3.3	0.054
P[l]	NAT	NAT	NAT	NAT	43	-[f]	-[f]	9.6	0.032
R	NAT	NAT	16.5	8.0	93[i]	-[f]	-[f]	-[f]	-0.068
S	-[f]	-[f]	NAT	NAT[m]	0[i]	NAT	NAT	-[g]	-0.017
T	NAT	2.3	46.5	NAT	0[i]	60.0	34.3	-[f]	0.020
U	NAT	NAT	NAT	12.1	0[i]	NAT	NAT	-[f]	0.065
V	NAT	NAT	36.0	9.4	0	-[f]	-[f]	94	-0.064
W	NAT	13.7	55.2	6.3	94[i]	37.5	19.6	50	0.031
X	NAT	4.8	NAT	NAT	0[i]	NAT	NAT	-[f]	0.047
Y	NAT	NAT	NAT	NAT	0	-[f]	-[f]	-[f]	-0.172
Z	NAT	NAT	NAT	42.0	10	-[f]	-[f]	-	-0.112

[a] No chemical mutagen was detected by the 10 microbial strains.

[b] No rat mortality after 14 days due to maximum dosage of 10^{-3} m^3/kg body weight (LD_{50}). However, six samples (B, C, F, L, N, and S) showed potential body weight effects, and sample B resulted in eye irritation.

[c] Effect was algal growth inhibition.

[d] Negative sign indicates inhibition in CO_2 generation rate compared to a control sample; positive number indicates CO_2 stimulation.

[e] No acute toxicity.

[f] Analysis not performed on this sample.

[g] Growth inhibition <50% in 100% solution of secondary effluent.

[h] pH = 9.1 not adjusted before testing.

[i] Sample stimulated algal growth.

[j] 95% growth inhibition in 2% solution of secondary effluent.

[k] Diseased batch of fish nullified this analysis.

[l] Sample inadvertently collected prior to settling pond.

[m] No statistical analysis because heavy solids concentration obscured the analysis; the sample did not appear to be acutely toxic.

TABLE 9. RELATIVE TOXICITY RANKING BY BIOASSAY TEST

Relative toxicity	Cytotoxicity (RAM)	Composite freshwater ecology (fathead minnow and *Daphnia*)	Composite marine ecology (sheepshead minnows, grass shrimp, and marine algae)	Clonal toxicity (CHO-K1)
Most toxic	C,N	N	L,N,T	D
		A,L		
		C,V		
Intermediate		W		
Toxicity	A,F,L,T,W,X, J	S	A,C,S,W	M,H,J
		U		
		T		
		G,R		
Least toxic	M	F,H,M	B,E,F,G,K,U,X	R,P,Y,Z
Nontoxic	B,E,G,K,U,D, H,P,R,V,Y, Z	B,K,E,X,D,J,P,'		
Not analyzed	S		D,H,J,M,P,R,V,Y,Z	A,B,C,E,F, G,K,L,N, S,T,U,V, W,X

Marine Ecology Series

Based on toxicity data for sheepshead minnows, grass shrimp, and marine algae, ranking of effluents by toxicity was accomplished and is shown in Table 9. In all samples, grass shrimp were more sensitive than sheepshead minnows. Also, the fathead minnows were more sensitive in all samples than sheepshead minnows. No general correlation was seen between the response of *Daphnia* and grass shrimp.

Cytotoxicity

Rabbit alveolar macrophage tests indicated that none of the samples was highly toxic. Two samples, N and C, were moderately toxic and the following seven samples were slightly toxic: L, W, T, X, A, F, and J.

Only eight samples were tested by MRC using the clonal toxicity test: D, H, J, M, P, R, Y, and Z. Of the eight samples, four showed significant toxicity: D, M, H, and J.

Mutagenicity

None of the 23 effluent samples produced a positive response in any of the bacterial tester strains. The Bioassay Subcommittee expressed concern that the detection limits for this bioassay series were not sensitive enough to detect the presence of significant concentrations (0.001 to 0.1 g/m^3) of chemical mutagens.

Rat Acute Toxicity Tests

No acute toxicity was observed from the maximum dose (10^{-5} m^3/kg) of rat body weight) ingested by the rats. However, six effluent samples showed potential body weight effects: F, N, C, L, S, and B. The subcommittee expressed concern about the detection limits of this test also.

Plant Ranking

Based on all of the above analyses, the subcommittee ranked the 23 textile plants in descending order of secondary effluent toxicity, and results are shown in Table 10.

TABLE 10. PRIORITIZATION OF TEXTILE PLANTS BY TOXICITY OF SECONDARY EFFLUENT

Toxicity ranking	Plant
Most toxic	N,A
	L,T
	C
	P,S
Least toxic	V,W,R
Nontoxic	B,D,E,F,G,H,J,K M,U,X,Y,Z

From the above list, the subcommittee recommended that the following nine textile plants be tested to determine the removal of toxicity achieved by the tertiary treatment technologies being tested in the ATMI/EPA Grant Study: N, A, L, T, C, P, S, W, and V. (Plant R was also recommended for study under Phase II because its secondary effluent samples were inadvertently collected prior to the settling pond.) In addition, they recommended that the freshwater ecology series be used to measure reduction in wastewater toxicity by the treatment technologies. The marine ecology series was not selected because none of the textile plants discharge wastewater into a marine environment.

Program Outline for Phase II Study

The objective of the second part of the textile wastewater toxicity study is to determine reduction in priority pollutant concentrations and in acute toxicity as a result of applying the ATMI/EPA BATEA tertiary treatment technologies to the secondary effluent at the 10 textile plants.

Pilot plants are scheduled to be at each (10) textile plant for from 6 wk to 8 wk. For the first 4 wk, seven tertiary treatment systems will be tested to determine which one provides the best removal of criteria pollutants. A treatment system consists of one or more of the six tertiary treatment technologies. From the data collected, the "best" system will be identified. This system will then be set up and operated at steady-state conditions for a final period of 2 wk.

For toxicity and priority pollutant analyses at each plant, 24-hr composited samples will be collected during the 2 wk of steady-state operations from the one system identified as the "best available technology." Since the tertiary treatment system will be composed of several of the six treatment technologies, samples will be collected before and after each unit operation in the system, resulting in approximately four samples.

In order to evaluate the reduction in toxicity and priority pollutant concentrations, 24-hr composited secondary effluent samples will also be collected. Due to hydraulic retention time through the pilot plant, secondary effluent sampling will lead the tertiary treatment sampling by the appropriate time for the tertiary treatment system selected.

A 24-hr composited sample of the intake water to the textile plant will be collected at each of the 10 plants to evaluate the source of priority pollutants in wastewater samples. Either continuous or grab samples will be collected depending upon the sampling conditions around the intake water facilities. Samples will be collected for volatile organics, nonvolatile organics, and metals analyses. Therefore, a total of approximately 6 samples will be collected at each of the 10 plants as illustrated in Table 11.

TABLE 11. SAMPLE SCHEDULE AT EACH OF THE 10 TEXTILE PLANTS

Sample site	No. of samples	Analyze for
Plant intake water	1	129 priority pollutants
Secondary effluent	1	129 priority pollutants and freshwater ecology series
Best tertiary treatment system	4	129 priority pollutants and freshwater ecology series

The freshwater ecology series consists of bioassay tests on the following three test organisms: fathead minnows, *Daphnia*, and freshwater algae. Five sample fractions are collected for priority pollutant analysis: volatile organics, nonvolatile organics, metals, cyanide, and phenol. Criteria pollutant analyses will not be performed since these analyses will be routinely performed under the ATMI/EPA Grant Study.

References

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Appendix A

Recommended List of Priority Pollutants

TABLE A-1. RECOMMENDED LIST OF PRIORITY POLLUTANTS

Compound name
Acenaphthene
Acrolein
Acrylonitrile
Benzene
Benzidine
Carbon tetrachloride (tetrachloromethane)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorobenzene
1,2,4-Trichlorobenzene
Hexachlorobenzene
Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)
1,2-Dichloroethane
1,1,1-Trichloroethane
Hexachloroethane
1,1-Dichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
Chloroethane
Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)
Bis(chloromethyl) ether
Bis(2-chloroethyl) ether
2-Chloroethyl vinyl ether (mixed)
Chlorianted naphthalene
2-Chloronaphthalene
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
2,4,6-Trichlorophenol
p-Chloro-*m*-cresol (4-chloro-3-methylphenol)
Chloroform (trichloromethane)
2-Chlorophenol
Dichlorobenzenes
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorobenzidine
3,3'-Dichlorobenzidine
Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)
1,1-Dichloroethylene (vinylidine chloride)
1,2-*Trans*-dichloroethylene
2,4-Dichlorophenol
Dichloropropane and dichloropropene

(continued)

TABLE A-1 (continued).

Compound name
1,2-Dichloropropane
1,3-Dichloropropylene
(*cis* and *trans*-1,3-dichloropropene)
2,4-Dimethylphenol
Dinitrotoluene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,2-Diphenylhydrazine
Ethylbenzene
Fluoranthene
Haloethers (other than those listed elsewhere)
4-Chlorophenyl phenyl ether
4-Bromophenyl phenyl ether
Bis(2-chloroisopropyl) ether
Bis(2-chloroethoxy) methane
Halomethanes (other than those listed elsewhere)
Methylene chloride (dichloromethane)
Methyl chloride (chloromethane)
Methyl bromide (bromomethane)
Bromoform (tribromomethane)
Dichlorobromomethane
Trichlorofluoromethane
Dichlorodifluoromethane
Chlorodibromomethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one)
Naphthalene
Nitrobenzene
Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)
2-Nitrophenol
4-Nitrophenol
2,4-Dinitrophenol
4,6-Dinitro-*o*-cresol
Nitrosoamines
N-nitrosodimethylamine
N-nitrosodiphenylamine
N-nitroso-di-n-propylamine
Penta chlorophenol
Phenol
Phthalate esters
Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-*n*-butyl phthalate
Diethyl phthalate

(continued)

TABLE A-1 (continued).

Compound name
Dimethyl phthalate
Di-n-octyl phthalate
Polynuclear aromatic hydrocarbons
Benz(a)anthracene (1,2-benzanthracene)
Benzo(a)pyrene (3,4-benzopyrene)
3,4-Benzofluoranthene
Benzo(k)fluoranthene (11,12-benzofluoranthene)
Chrysene
Acenaphthylene
Anthracene
Benzo(ghi)perylene (1,12-benzoperylene)
Fluorene
Phenanthrene
Dibenz(ah)anthracene (1,2,5,6-dibenzanthracene)
Indeno(1,2,3-cd)pyrene (2,3-*o*-phenylenepyrene)
Pyrene
Tetrachloroethylene
Toluene
Trichloroethylene
Vinyl chloride (chloroethylene)
Pesticides and metabolites
Aldrin
Dieldrin
Chlorodane (technical mixture and metabolites)
DDT and metabolites
4,4'-DDT
4,4'-DDE (p,p'-DDX)
4,4'-DDD (p,p'-TDE)
Endosulfan and metabolites
α-Endosulfan
β-Endosulfan
Endosulfan sulfate
Endrin and metabolites
Endrin
Endrin aldehyde
Heptachlor and metabolites
Heptachlor
Heptachlor epoxide
Hexachlorocyclohexane
α-BHC
β-BHC
λ-BHC (lindane)
δ-BHC

(continued)

TABLE A-1 (continued).

Compound name
Polychlorinated biphenyls (PCB)
PCB-1242 (Arochlor 1242)
PCB-1254 (Arochlor 1254)
PCB-1221 (Arochlor 1221)
PCB-1232 (Arochlor 1232)
PCB-1248 (Arochlor 1248)
PCB-1260 (Arochlor 1260)
PCB-1016 (Arochlor 1016)
Toxaphene
Elements
Antimony (Total)
Arsenic (Total)
Asbestos (Fibrous)
Beryllium (Total)
Cadmium (Total)
Chromium (Total)
Copper (Total)
Cyanide (Total)
Lead (Total)
Mercury (Total)
Nickel (Total)
Selenium (Total)
Silver (Total)
Thallium (Total)
Zinc (Total)
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

NONFERROUS METALS PROCESSING
(COPPER REVERBERATORY FURNACES)

by

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Abstract

This paper provides information on an application of environmental assessment testing for a selected number of copper smelters as an example of the nonferrous metal processing industry. Details are provided regarding the sampling methodology and subsequent analysis techniques used to characterize the effluents for hazardous toxic emissions. A discussion is provided regarding the results of the findings in terms of the quantities of emissions expected and the potential errors of measurement. Some specific toxic emissions were found to be present in substantial quantities. Also presented is information regarding the difficulties attendant to sampling smelter effluent streams.

Introduction

The nonferrous metals industry produces metals, such as aluminum, copper, lead, zinc, and nickel, by various hydrometallurgical and pyrometallurgical techniques. The prime objective is recovery of the base metal and elimination of extraneous by-products and wastes. In the pyrometallurgical systems, the raw materials are subjected to high-temperature processes which may involve selective oxidation, reduction, volatization, melting and slagging to separate the waste materials from the valuable nonferrous metals. The high processing temperatures result in evolution of large volumes of off-gases containing large amounts of particulate matter, much of which is metallic compounds in the "fine particulate" range. Since many of the nonferrous minerals are associated with sulfur, the off-gases frequently contain SO_2, SO_3, and sulfuric acid mist along with the particulate matter. To further complicate the problem, at the high processing temperatures involved, some metals such as arsenic, cadmium, zinc, mercury, and selenium are volatilized and become part of the pyrometallurgical off-gases. Other materials such as fluorine and phosphorous may also be volatilized.

For those off-gases containing large amounts of SO_2, production of by-product sulfuric acid, liquid SO_2, or elemental sulfur may be technically and economically feasible, and extensive measures are taken to remove particulate matter before processing the gas stream. However, whether the gas stream is to be processed for by-product recovery or not, particulate matter is normally removed by electrostatic precipitators, fabric filters, and various types of scrubbers. Depending on the composition of the recovered particulate, it may be either recycled to the process or disposed of as solid waste.

Within the nonferrous industry, one cannot safely generalize on the type of particulate control equipment which should be used, and many combinations of electrostatic precipitators, fabric filters, and scrubbers are used depending on the particular raw material or process requirements, the secondary pollution problems (such as scrubber purges causing wastewater problems), the type pollutant to be controlled, and comparative capital and operating costs. Recognizing the danger in generalizations, wet electrostatic precipitators are widely used in the aluminum industry to control emissions from reduction cells; dry electrostatic precipitators are used in primary copper smelters on roasters, reverberatory and electric furnaces, and converters; fabric filters are used on primary lead updraft sinter machines and blast furnaces; and electrostatic precipitators are used on zinc roasters and downdraft sinter machines. There are numerous exceptions to all of these generalizations; however.

Since there are many unknowns regarding performance of control devices on metallurgical off-gases, EPA's Metals and Inorganic Chemicals Branch initiated a program to obtain the necessary information to evaluate performance of control devices such as electrostatic precipitators. Southern Research Institute has been involved in research on electrostatic precipitators for a number of years under EPA sponsorship, and one of our current programs being sponsored by EPA's Cincinnati Industrial Environmental Research Laboratories is concerned with the evaluation and control of particulates from nonferrous smelting operations, with particular emphasis on ESP's.

Copper Smelter Tests

The first industry selected for study under this program was the primary copper smelting industry. Limited mass and particle size distribution measurements were conducted across electrostatic precipitators collecting particulates from the effluent gas streams from two primary copper reverberatory furnaces.

The first field test served as an opportunity to evaluate the particulate test methods that had been developed and used extensively on coal-fired utility applications for use in the nonferrous metals industry. Since the effluent gas stream from a copper reverberatory furnace differs markedly from that of a coal-fired utility, this evaluation was thought to be necessary.

The second field test was expanded significantly from the first test in an effort to obtain a larger data base for use in this research program. This test was also conducted on an electrostatic precipitator operating on a reverberatory furnace off-gas.

A simplified flow diagram of a typical copper smelter is shown in Figure 1. The raw ore from the mine is beneficiated to obtain a concentrate which typically contains 20 to 25 percent copper with associated iron, sulfur, and minor elements. The concentrate is usually received at the smelter as a slurry or wet cake. In a typical process scheme, the concentrate may be partially roasted to eliminate some sulfur and to provide a dry calcine as feed to the reverberatory furnace. Autogenous roasting is usually carried out at about 1150-1200°F, and the off-gases usually contain enough SO_2 for efficient conversion to sulfuric acid. The reverberatory furnace requires an external fuel source, such as natural gas, fuel oil, or coal, and is operated at about 2200-2500°F. The primary functions of the reverb are to provide a balanced Cu-Fe-S matte for feed to the converter while removing extraneous Fe, SiO_2, etc. as slag. Normally, off-gases from the reverberatory furnace are low in SO_2 and are most frequently vented to the atmosphere after removal of particulate matter. The converters are also operated at about 2200-2500°F on a cyclic basis to obtain a product blister copper and an iron slag which is normally recycled to the

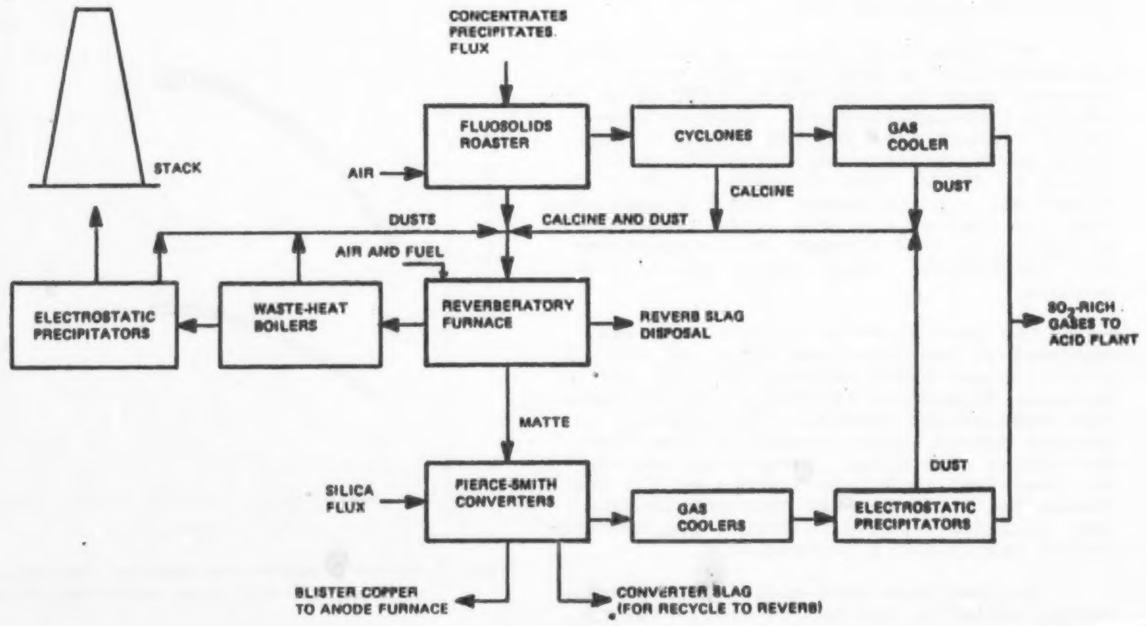

CONCENTRATES
PRECIPITATES
FLUX
STACK
AIR
FLUOSOLIDS ROASTER
CYCLONES
GAS COOLER
CALCINE
DUST
DUSTS
CALCINE AND DUST
AIR AND FUEL
ELECTROSTATIC PRECIPITATORS
WASTE-HEAT BOILERS
REVERBERATORY FURNACE
REVERB SLAG DISPOSAL
SO_2-RICH GASES TO ACID PLANT
MATTE
DUST
SILICA FLUX
PIERCE-SMITH CONVERTERS
GAS COOLERS
ELECTROSTATIC PRECIPITATORS
BLISTER COPPER TO ANODE FURNACE
CONVERTER SLAG (FOR RECYCLE TO REVERB)

Figure 1. Simplified Flow Diagram of Copper Smelter.

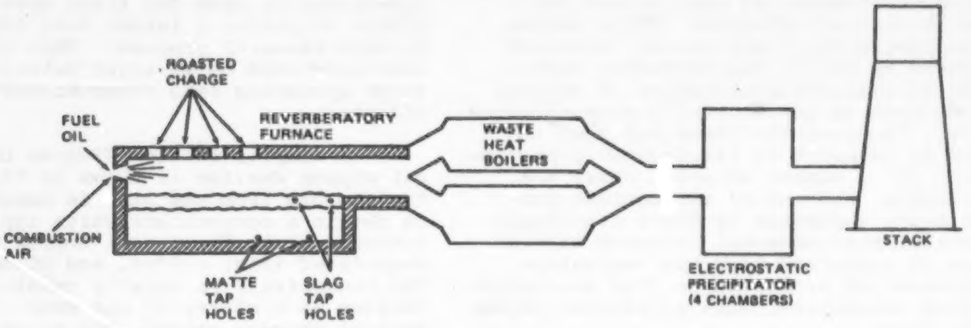


Figure 2. Reverberatory Furnace Schematic

reverberatory furnace. Converter off-gases have highly cyclic flow patterns, but the SO_2 content is usually high enough for processing to acid.

Since off-gases from the reverberatory furnaces are most often vented to the atmosphere, our first field tests were logically focused on ESP's associated with reverbs. In one case, the feed to the reverberatory furnace was a partially roasted calcine; in the other, the feed was a dried but unroasted concentrate. Otherwise, operation of the two units was quite similar and is illustrated in Figure 2. Both units were equipped to use either natural gas or fuel oil, and both have waste-heat boilers preceding the ESP's.

The mass tests across the ESP's were conducted with an ASME-type mass train inserted into the flue and maintained at near in-line temperatures. This is somewhat different from the EPA Method 5 test, in which the filter temperature is maintained at 250°F. The in-stack filter method was used to assure that the particulate captured in the mass train actually entered or passed through the precipitator as a particulate rather than a gas or condensate.

The particle-size distribution was measured at the inlet and outlet of the precipitators using cascade inertial impactors, five-stage cyclones, and two real-time measurement systems. The inertial systems provide time-integrated size distributions with time. These test methods are described in a report prepared for the Industrial Environmental Research Laboratory entitled *Procedures Manual for Electrostatic Precipitator Evaluation*.

Gas analyses were made at the precipitator outlet at various intervals during the test period. Since it was anticipated that the sulfur oxide content would vary during reverb operation, samples were taken immediately before and after charging periods as well as during quiescent stages of the operation.

The descriptive parameters for one of the precipitator installations is given in Table 1, and the test results are described in Tables 2 and 3 and Figure 3.

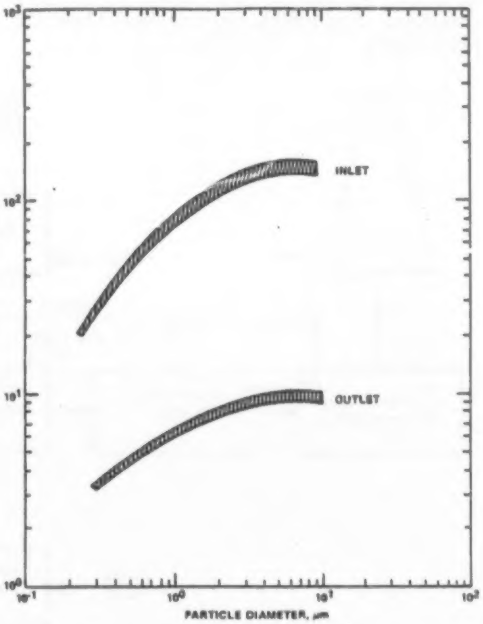


Figure 3. Average cumulative inlet and outlet mass loading vs. particle size, Plant A copper reverberatory furnace.

TABLE 1. ELECTROSTATIC PRECIPITATOR DESCRIPTIVE PARAMETERS, REVERBERATORY FURNACE FOR PLANT A

Item	English	Metric
Collection electrode area (A)(total-2 ESP)	39744 ft^2	3692.4 m^2
Inlet set area (power set C)	19872 ft^2	1846.2 m^2
Outlet set area (power set A)	9936 ft^2	923.0 m^2
Outlet set area (power set B)	9936 ft^2	923.0 m^2
Collection electrode spacing	9 in.	0.229 m
Corona electrode diameter (round wire)	0.1055 in.	2.7 mm
Collection electrode dimension	9 ft x 24 ft	2.74 m x 7.32 m
Number of gas passages (total - 2 ESP)	46	
Gas passage length (active)	18 ft	5.49 m
Volume flow rate design (V)	150,000 acfm	70.8 m^3/sec
Design temperature	600-700°F	315-371°C
Design efficiency	96.83%	
Design precipitation rate parameter (w)	0.21 ft/sec	6.5 cm/sec
Specific collection electrode area (A/V)	265 ft^2/ 1000 cfm	52 m^2/m^3 sec

TABLE 2. MASS CONCENTRATIONS AND EFFICIENCY, PLANT A

Mass Concentration				Efficiency, %	
Inlet mg/DSCM		Outlet mg/DSCM			
Impactor	Mass Train	Impactor	Mass Train	Impactor	Mass Train
1146	1407	41	48	96.4	96.6
641	1304	21	41	96.7	96.8

TABLE 3. SULFUR OXIDE CONCENTRATIONS, PLANT A

Sampling Rate, l/min	Furnace Charge Cycle	% By Volume	
		SO_2	SO_3
3.2	after	1.0	0.024
2.9	before	0.42	0.019
2.4	after	0.73	0.018
1.9	before	0.63	0.025
1.0	after	1.7	0.067

The operation of the precipitator was within design specification, and no major operating problems were encountered during the test period. The overall efficiency based on impactor and mass-train data (Table 2) ranged from 96.4 percent to 96.8 percent versus the design efficiency of 96.8 percent. The fractional efficiency for "fine particulate" showed an expected characteristic decrease in the 0.5 to 1.0 μm range.

As a part of our field study of the two precipitators operating on copper reverberatory furnaces, we also investigated the fate of some of the minor elements of environmental concern. Samples were collected from the gas streams with a wet-electrostatic-precipitator train, a series of external impingers, cyclone separators, and glass-fiber thimbles. Most elemental analyses were made using a spark-source mass spectrometer and atomic absorption. Fluorine content was determined with an ion-selective electrode, and selenium was determined by a fluorometric procedure.

The screening analyses identified the presence of over fifty elemental species; however, most of the evaluation was concerned with the 19 elements shown in Table 4. For the minor elements listed, only arsenic, fluorine, mercury, and perhaps chromium, selenium, antimony, and molybdenum are present as vapors or ultrafine particulate at the ESP outlet for this particular smelter. The remainder are either caught by the ESP or leave the process as a scrubber-water purge or as slag waste. For the tests in question, only arsenic and fluorine were present in the ESP outlet in significant quantities above 1 lb/hr as shown in Table 5. Since fluorine from the reverb exists in some gaseous form, probably as SiF_4, it would not be caught by the ESP or a fabric filter, and most of the fluorine entering the smelter would probably leave in the off-gas from the reverb ESP.

TABLE 4: ELEMENTS IN REVERBERATORY FURNACE

Aluminum (Al)
Arsenic (As)
Barium (Ba)
Beryllium (Be)
Calcium (Ca)
Cadmium (Cd)
Chromium (Cr)
Copper (Cu)
Fluorine (F)
Iron (Fe)
Mercury (Hg)
Molybdenum (Mo)
Nickel (Ni)
Lead (Pb)
Antimony (Sb)
Selenium (Se)
Silicon (Si)
Vanadium (V)
Zinc (Zn)

TABLE 5: QUALITATIVE DISTRIBUTION OF ELEMENTS ACROSS REVERB AND PRECIPITATOR

Inlet Feed

Greater than 1000 lbs/hr - Cu, Fe, Si
100 to 1000 lbs/hr - Al, As, Ca
10 to 100 lbs/hr - Ba, Cd, Mo, Pb, Se, Zn
1 to 10 lbs/hr - F, Sb
Less than 1 lb/hr - Be, Cr, Hg, Ni, V

Outlet Off-Gases

Greater than 10 lbs/hr - As
1 to 10 lbs/hr - Cu, F, Si
0.1 to 1 lb/hr - Al, Ba, Fe, Mo, Pb, Se, Zn
Less than 0.1 lb/hr - Be, Ca, Cd, Cr, Hg, Ni, Sb, V

Arsenic, which was the predominant volatile metal in the feed to the copper reverberatory furnaces, was partially caught in the ESP operating above 500°F; however, a large part of the arsenic remained in the ESP outlet. An approximate arsenic balance over the entire smelter system is given in Table 6. For this particular smelter, a small amount of the arsenic remains in the copper product and will eventually be removed in electrolytic refining of the copper. About half of the arsenic ends up in the reverberatory-furnace slag and the acid-plant-purge water, about equally divided between the two. The remainder of the arsenic, nearly 50 percent, is not caught by the hot ESP and is vented to the atmosphere.

TABLE 6: APPROXIMATE ARSENIC DISTRIBUTION

Reverb Slag	25 - 30%
Acid Plant Purge Water (Converter off-gases)	25 - 30%
Blister (or Anode) Copper	5%
Reverb ESP Outlet	40 - 45%

Referring back to Figure 1, we can make a few qualitative observations on arsenic and some of the other volatile minor elements that may be found in the copper-smelting system. At the operating temperatures of most roasters (1150°-1200°F), very few of the elements or their oxides or sulfides are volatile. Some arsenic, mercury or fluorine could be evolved but probably in insignificant amounts. At the operating temperatures in the reverberatory furnace and converter (2200-2500°F), a number of metals and oxides may be volatilized including arsenic, antimony, barium, cadmium, lead, mercury, molybdenum, rhenium, and selenium in addition to fluorine and phosphorus. Some of the minor elements such as molybdenum end up in the reverberatory furnace slag, and some may end up in either the slag or in the acid-plant-purge water.

However, since both the slag from the reverberatory furnace and the acid-plant-purge water are waste streams from the smelter and could constitute environmental problems if the arsenic and other toxic metals are not bound in an innocuous form. The arsenic, fluorine, and other minor elements leaving the stack may also constitute a potential environmental problem and health hazard.

Additional research is needed to develop a better understanding of the minor-element emissions from nonferrous smelters and to improve the control systems if adverse environmental and health effects are found. We do not represent our limited findings as identifying a widely recurrent circumstance, and it should be recognized that the minor-element emissions will vary widely from one smelter to another. However, we believe that further investigation of these minor-element emissions and their control is warranted.

Acknowledgments

We would like to acknowledge Radian Corporation for their collaboration with Southern Research Institute on these studies, especially Dr. Klaus Switzgebel and Mr. Robert V. Collins. We also appreciate the cooperation of the management and personnel at the two copper smelters, and the support of EPA through Mr. George S. Thompson, Jr. and our project officers, Ms. Margaret Stasikowski and Mr. John O. Burckle.

APPLICATION OF THE PHASED APPROACH TO ENVIRONMENTAL ASSESSMENT TO THE EMISSION ASSESSMENT OF CONVENTIONAL COMBUSTION SERVICES

By

J. Warren Hamersma

Abstract. The EPA program concerning the Emissions Assessment of Conventional Combustion systems is the first large scale application of the phased approach for environmental assessment. This program includes the evaluation of 170 sites in 50 source categories grouped in 5 general areas. These are residential, internal combustion, electrical generation, commercial/institutional and industrial sources. The major emphasis is on the application of Level 1 sampling and analysis techniques to this program and the integrated decision criteria that have been developed for the cost effective attainment of the program's objectives. Also included is a discussion of the program, its goals, some unique problems, and a general discussion of some of the results to date.

Introduction. The major objective of this program is to assess air and water pollutants generated by conventional stationary combustion systems including pollutants from related solid waste disposal. This includes the identification and quantification of both criteria and noncriteria pollutants using Level 1 methods as well as acquiring some Level 2 or quasi-Level 2 data as required in the statement of work. This objective is being implemented in four general steps. First, criteria were developed to determine the adequacy of existing emissions data. In doing this, the available data were screened for definition of process and fuel parameters as well as for the validity and accuracy of the sampling and analysis methods. The acceptable emissions data were than subjected to an engineering and statistical analysis. Then after discarding the outliers, the mean and variability in the emission factors are calculated. Second, this information is then used in a continuing process to identify parts of or whole emission source categories that have been adequately assessed, and to specify those categories that require additional investigation. Finally, a test program has been developed to complete the emission assessment. In a sense this process is the heart of the program in that it provides the focus for both the sampling and analysis effort.

Present Status. The overall status of the planning and assessment task can be summarized as follows:

- Criteria for assessing the adequacy of the emissions data base have been developed,
- A source type sampling plan has been prepared,
- A preliminary evaluation of existing emissions data base has been completed,
- Additional emissions data from recently completed and on-going projects are being evaluated,
- Draft reports on emissions from residential oil and internal combustion units have been submitted to EPA, and
- Finally, additional data on source characteristics, including size and age distribution, market trends, current and future comsumption, are being compiled.

The source type sampling plan is in a constant state of evolution. In total, 50 source sub-categories are being considered which can be grouped into 5 general categories shown in Table 1. The factors that were considered in preparing this plan included grouping of certain source sub-categories, the latest fuel usage trends, equipment obsolescence, and general data base quality. For each of the subcategories in the general groupings, 5 test sites are considered adequate for determining if additional Level 1 or Level 2 testing will be required.

Sampling. In order to carry out the sampling portion of this program, two complete sampling vans have been constructed. One operates on the West Coast and the other on the East Coast. The vans are divided into two general areas. The forward area contains an icemaker to partially supply ice for the SASS train, gas bottles for the gas chromatographs, and a water purification unit. In addition there is space to assemble and disassemble the SASS train components. This area is segregated from the rear part of the van so that dust and contamination carried into the van with the SASS train and other equipment will not contaminate the sample when it is recovered. The rear part of the van is maintained as a clean area and contains bench space for SASS train sample recovery, on site analysis, and miscellaneous work-up of the other samples prior to shipment. Two gas chromatographs are used. One has a thermal conductivity detector and is used for analysis of the inorganic gases O_2, CO, CO_2, and N_2. The second has a flame ionization detector and is used to analyze the C_1-C_6 hydrocarbons. In addition, there is a laminar flow bench and a fume hood to aid in on site analysis and sample preparation. A schematic of the van is given in Figure 1.

In terms of field sampling, there are two general areas where additional procedural guidelines are needed. Although operating conditions for the SASS train are fairly well established, there are no firm guidelines as to what is an acceptable Level 1 sampling port. On a program such as this where a large number of sources are to be tested, there are not an unlimited number of sites from which to chose and some compromises must be made. In addition, sampling after a control device gives a better indication of actual emissions, while sampling before a control device probably gives a better indication of boiler operating conditions which can affect these emissions. In addition to this problem, a general protocol or program specific protocol must be developed in terms of what streams should be sampled and where they should be sampled. For instance, if several different units are interconnected, where do you sample cooling water, ash streams, and other miscellaneous waste streams? The actual decision can make an enormous difference in the number of samples and subsequent analysis costs. Presently these decisions are being made on a case by case basis.

General Decision Criteria. In terms of overall decision criteria, the planning and assessment analysis plan is the most important. As a result of this plan specific sample types or parts of the sampling train will be deleted if sufficient data exists or will be available.

For instance,

- TVA is studying coal pile drainage
- There are separate programs for studying fugitive emissions and ash pound drainage from utility plants
- Certain water data is available and other water discharges can be calculated.
- Cooling tower emissions have been defined as independent of boiler type and are being assessed as a separate task.

Field Sampling and Analysis Decision Criteria. The general EPA Level 1 guidelines have been supplemented based on the general sampling requirements of the combustion source assessment programs. Many of the combustion sources are known or projected to have low gain loadings and the expected cyclone catchers will be very low. Based on available data, it has been possible to estimate in a very conservative manner the $>3\mu$ and $<3\mu$ catches as a function of grain loadings for coal, residual oil, distillate oil, gasoline, diesel fuel, and natural gas fired units. For coal fired units, the effect of control devices at lower grain loadings was taken into effect. The general curve shown in Figure 2 takes into account all fuel and control device variations so that the greater than 3μ catch is always conservatively estimated on the high side. Based on this curve, a series of cyclone deletion guidelines in Table 2 have been developed that allows the deletion of one or more cyclones. This allows labor saving in terms of set-up and sample recovery time when little or no sample will be collected. This also has the technical advantage of allowing the collection of samll amounts of sample that would be lost if spread over one or more cyclones as well as preventing the concomitant higher levels of contamination that occur in the recovery of samll amounts (less than 6 mg) of material in the field. Table 3 shows the expected application of these guidelines as a function of fuel type. It should be emphasized that these projections are in the process of being verified but that present data indicates that the information presented is applicable and sufficiently conservative.

Fugitive emissions assessment is normally part of a Level 1 assessment. However, in the case of combustion sources several studies are now underway to assess the problem. For this reason, this effort was dropped because the expected data will supply the needs of the program. The field crews do carry detector tube kits for use when obvious problems exist.

Laboratory Analysis Decision Criteria. If all Level 1 analyses were attempted on all samples regardless of the expected data output, the program cannot be accomplished in a cost effective manner. For this reason, the Level 1 analysis decision criteria have been supplemented in order to limit the analyses in these samples that will provide new and useful data. These criteria involve both inorganic and organic analysis.

The first set of decision criteria involves small particulate catches. If after combining the filter and cyclone catches into greater than and less than 3μ functions, the sample is less than 10 mg no analyses are performed; if it is between 10 and 100 mg, SSMS analysis only is performed; if it is between 100 and 150 mg, SSMS as well as Hg, Sb, and As analysis are performed; and if it is greater than 150 mg organic analysis is added. In many cases, solids are collected in the SASS train probe rinse. These are subjected to separate analysis by the above criteria only if this quantity is greater than 10% of the total catch.

When distillate fuels are used in units tested on this program, it can be expected that the inorganic element content can be defined within rather narrow limits. A careful review of the literature and actual fuel analysis indicate that deviations from site to site are statistically insignificant within the limits of Level 1 accuracy, thus further analyses will no longer be performed on the remaining sites using these fuels.

During the course of the program, the Level 1 organic analysis scheme was modified in order to allow for a more nearly accurate analysis of C_7-C_{16} material. Much of this material is lost in the original Level 1 organic analysis, so the analysis was modified by IERL's Process Measurements Branch to include a total chromatographable organic analysis (TCO) on the bulk samples and all liquid chromatography (LC) fractions. Because this addition could add up to eighty additional gas chromatographic analysis per site, a set of decision criteria were set up in order to perform only those analysis that could be expected to yield useful data. Thus if the TCO is greater than 10% of the total organics, the analysis scheme (Method 1, Fig. 3) using solvent exchange and TCO on all LC fractions is followed. If the TCO is less than 10% of the total organics, the original Level 1 analysis scheme (Method 2, Fig. 3) is followed. If the total organics is less than 500 mg/M^3, the organic analysis is terminated per Level 1 criteria. Because of the large number of infrared analysis (IR) that must be performed on this program, lower limits for IR analysis were adopted to limit the number of IR analysis that provide no useful information. Thus IR spectra are not obtained on samples less than 0.5 mg for the bulk residues and 1 mg for LC fractions. The above and other basic organic analysis decision points are summarized in Table 4.

Table 1. Source Type Sampling

General Source Category	No. of Sites
Residential sources	16
Internal combustion sources	11
Electricity generation external combustion sources	51
Commercial/institutional sources	53
Industrial sources	30
Total committed sites	161
Total unassigned sites in reserve pool	9
Total Level 1 sites	170

TABLE 2. SASS Train Cyclone Use Criteria*

Grain Loading	Projected Catch g		Cyclones Required		
	>3μ	<3μ	1μ	3μ	10μ
>0.11	>.006	>6.9	Yes	Yes	Yes
0.051-0.10	.004-.006	3.1-6.9	Yes	Yes	No
0.021-0.050	nil	1.4-3.1	Yes	No	No
0.0001-0.020	nil	0.007-1.4	No	No	No
<0.0001	nil	<.007	Run XAD-2 module and impingers only		

*A filter is used in all cases.

TABLE 3. Expected Application of SASS Train Cyclone as a Function of Fuel Type*

Fuel Type	Projected Grain Loading	Cyclones Required		
		1μ	3μ	10μ
Coal	>0.1	Yes	Yes	Yes
Residual Oil	0.051-0.10	Yes	Yes	Yes
	0.021-0.05	Yes	No*	No
	<0.020	No	No*	No
Distillate Oil	<0.02	No	No*	No
Natural Gas	<0.02	No*	No	No
Gasoline	<0.02	No*	No	No
Diesel Fuel	<0.02	No*	No	No

a) A filter is to be used in all cases.
*This cyclone will be used until field tests show that it is not necessary.

TABLE 4. Organic Analysis Decision Points

Decision Point	Description
Initial Extraction	Organic analysis omitted if quantity of particulate catch is limited and/or meets certain criteria (see below).
Gravimetric Analysis	a) Analysis terminated if organics concentration is <0.5 mg/m^3 b) Analysis on the XAD-2 condensate is discontinued if nonvolatile matter <10% of total organics or <0.5 mg/m^3.
Total Chromatographable Organics, C_7-C_{16} (TCO)	Simplified liquid chromatographic (LC) separation used if TCO <10% total organics.
Infrared Analysis	Analysis not run on less than 0.5 mg for basic gravimetric residues, or 1 mg for LC fractions.
Low Resolution Mass Spectroscopy	Run only on total residues or LC fractions, if present in concentrations of >0.5 mg/m^3.
POM Analysis	Performed only on fractions showing >0.5 mg/m^3 organics.

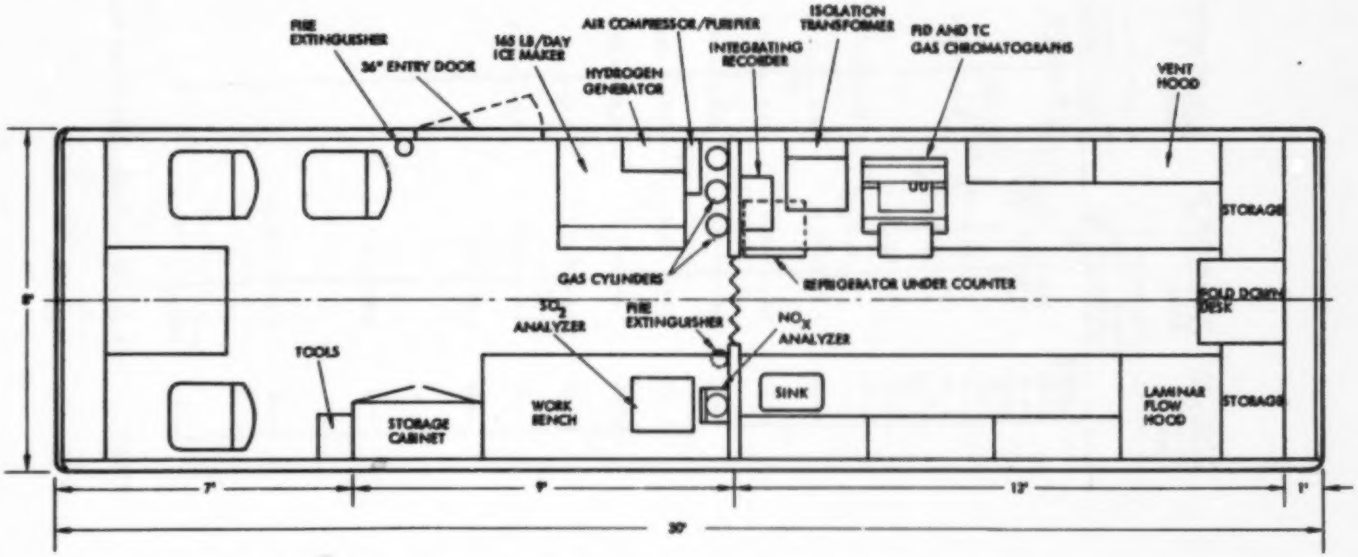

FIRE EXTINGUISHER
36" ENTRY DOOR
165 LB/DAY ICE MAKER
HYDROGEN GENERATOR
AIR COMPRESSOR/PURIFIER
INTEGRATING RECORDER
ISOLATION TRANSFORMER
FID AND TC GAS CHROMATOGRAPHS
VENT HOOD
STORAGE
GAS CYLINDERS
REFRIGERATOR UNDER COUNTER
FOLD DOWN DESK
SO_2 ANALYZER
FIRE EXTINGUISHER
NO_X ANALYZER
TOOLS
STORAGE CABINET
WORK BENCH
SINK
LAMINAR FLOW HOOD
STORAGE
8'
7'
9'
12'
1'
30'

FIGURE 1. Schematic of Environmental Assessment Sampling Van

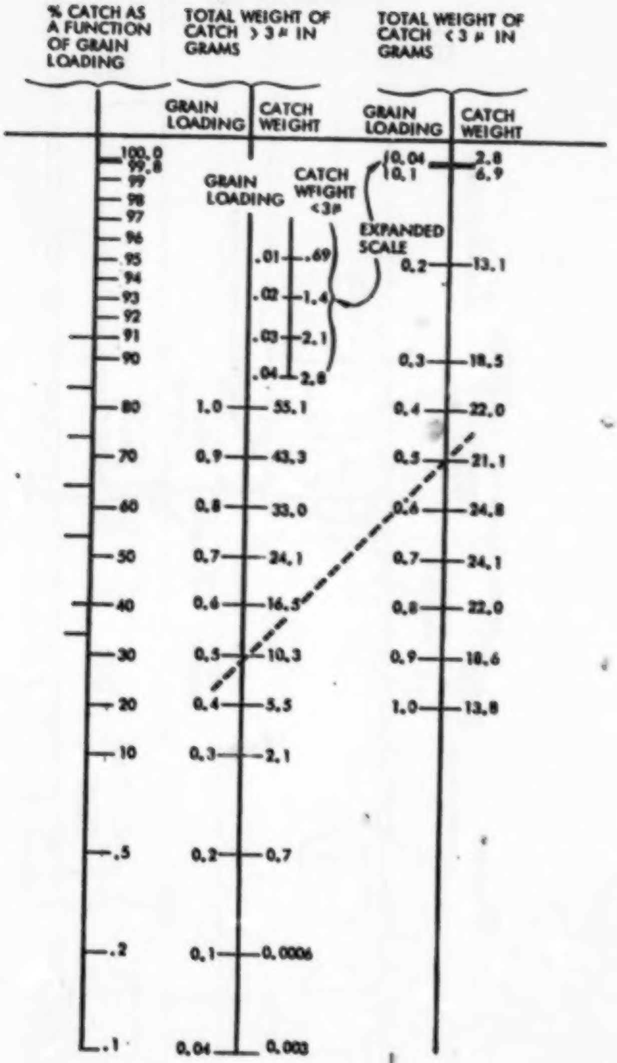
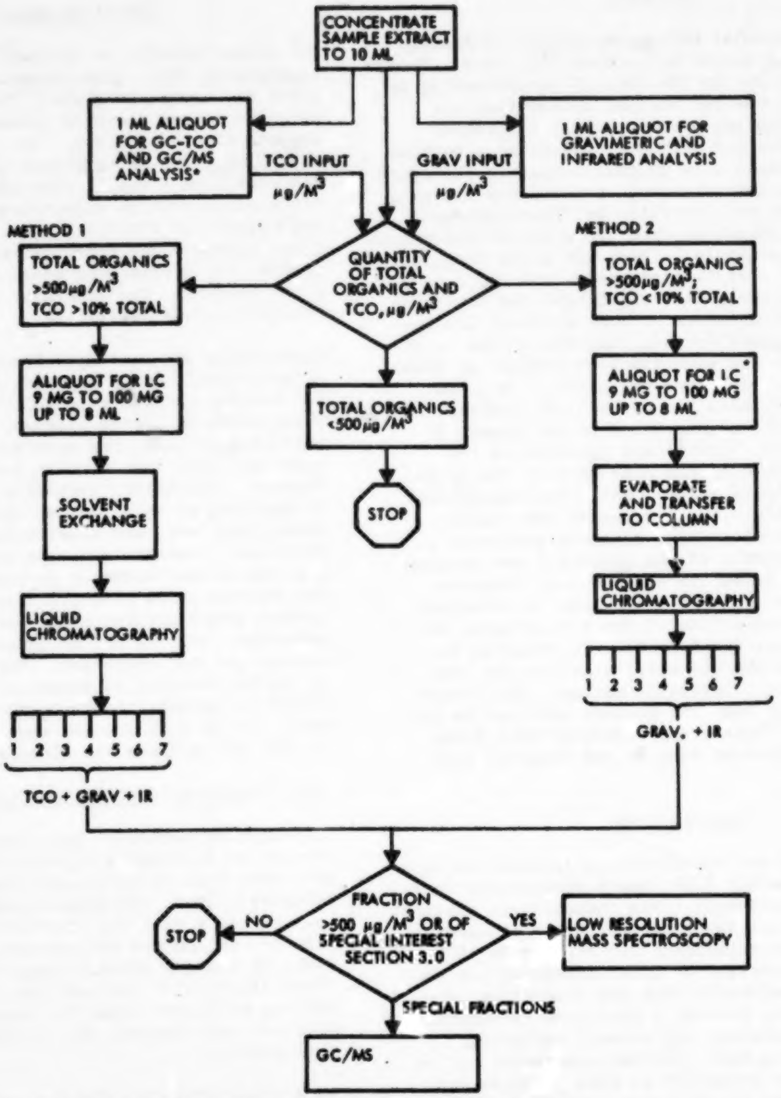


FIGURE 2. Particulate Analysis Prediction Nomograph


CONCENTRATE SAMPLE EXTRACT TO 10 ML
1 ML ALIQUOT FOR GC-TCO AND GC/MS ANALYSIS*
1 ML ALIQUOT FOR GRAVIMETRIC AND INFRARED ANALYSIS
TCO INPUT μg/M^3
GRAV INPUT μg/M^3
METHOD 1
METHOD 2
QUANTITY OF TOTAL ORGANICS AND TCO, μg/M^3
TOTAL ORGANICS >500μg/M^3 TCO >10% TOTAL
TOTAL ORGANICS >500μg/M^3; TCO <10% TOTAL
TOTAL ORGANICS <500μg/M^3
STOP
ALIQUOT FOR LC 9 MG TO 100 MG UP TO 8 ML
ALIQUOT FOR LC* 9 MG TO 100 MG UP TO 8 ML
SOLVENT EXCHANGE
EVAPORATE AND TRANSFER TO COLUMN
LIQUID CHROMATOGRAPHY
LIQUID CHROMATOGRAPHY
1 2 3 4 5 6 7
1 2 3 4 5 6 7
TCO + GRAV + IR
GRAV. + IR
FRACTION >500 μg/M^3 OR OF SPECIAL INTEREST SECTION 3.0
NO
YES
STOP
LOW RESOLUTION MASS SPECTROSCOPY
SPECIAL FRACTIONS
GC/MS

*GC - GAS CHROMATOGRAPHY; TCO - TOTAL CHROMATOGRAPHABLE ORGANIC MATERIAL; LC - LIQUID CHROMATOGRAPHY; MS - MASS SPECTROSCOPY.

FIGURE 3. Organic Analysis Scheme

EMISSIONS FROM THE GLASS MANUFACTURING INDUSTRY

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B. Blakeslee, Scott Environmental Services
R. Barrett, Battelle, Columbus, OH

Abstract

The introduction of pollution control technology into the glass industry has been very slow. This was primarily due to the lack of understanding of the nature of the gas streams coming from the glass manufacturing process. Past assessment studies of this industry have indicated a serious lack of emissions data on this industry; therefore, to provide an understanding of these gas streams, a test program was initiated by IERL-Cincinnati to characterize emissions from the glass manufacturing process and particularly from the glass furnaces. Ten different installations were selected consisting of furnaces in the 200 tons per day range. The test results indicated that although low in-opacity, the glass furnace emission stream is of complex nature and should not be considered free of potentially dangerous pollutants. SO_x, NO_x and toxic heavy metals such as lead, arsenic, selenium and cadmium were found to be present in the gas stream. Significant portions of the metals were found in the back half of the Method 5 train indicating either their vaporous or fine particulate nature as they passed the filter. Finally, particulate size analysis indicated a significant portion of the potential particulate matter may be below the minimum size range at which classical control technology is efficient. Preliminary conclusions of the test program indicate that additional testing is required to further define the characteristics of the fine particulate and condensible matter. This would require testing near the furnace exit and in the regenerators. These areas represent more harsh testing environments than in the original test program.

Introduction

The domestic glass manufacturing industry is made up of approximately 1000 plants producing a variety of glass products. This industry was assigned to the Industrial Environmental Research Laboratory to conduct assessment R&D efforts in 1976. The primary objective of this assessment was to characterize emissions from the production processes and thus, provide a data base to support future EPA regulatory and control technology development programs. Initial assessment activities conducted primarily as paper studies indicated data gapes in available literature and research information. Therefore, as a continuation of the industry assessment program, an emissions testing program was initiated to quantify emissions and fill the data gaps identified by assessment studies.

The Glass Industry

The glass industry is divided into three major segments by EPA: flat glass, pressed and blown glass and container glass. The major production of glass in the domestic industry is in container segment of the industry. Over 70% of the total U.S. production is container glass and is primarily soda lime glass.[1] Flat glass and pressed and blown glass make up approximately 19% and 11%, respectively, of the total U.S. production.[2] The glass industry has approximately 140 container plants, 260 pressed and blown plants and 75 flat glass plants. The remainder is made up of small specialty glass facilities.

Glass types are usually defined by their major oxide constituent. They include: sodium oxide and calcium carbonate in soda-lime glasses and boric oxide in borate glasses. During the manufacturing process, raw materials are batched, mixed and injected, usually into a fossil-fired furnace. The batch, typically, consists of silica in the form of sand, cullet (recycled glass), limestone, soda ash, and alumina-bearing materials. There are, however, numerous other materials which are used either alone or in combination to produce the desired glass product. Figure 1 outlines a typical glass manufacturing process. In terms of emissions, melting can be considered the most important process operation. The furnaces are typically elevated to temperatures in excess of 1500°C to produce the homogeneous molten glass mass. It is this process that the major emphasis of the test program was directed.

The Glass Manufacturing Assessment Test Program

The major objective of any laboratory assessment program is to develop a qualitative and quantitative data base on pollutants from the affected industry. Thus, the glass manufacturing assessment has as a goal the identification and determination of sources and characteristics of pollutants from glass process operations: this includes identification of chemical species as well as quantifying pollutant emission rates and determining physical and chemical characteristics of the pollutants.

Nine plant sites involving eleven different furnaces were selected as sources of the data. These sites were selected based upon type of glass produced, quantity of glass produced and their similarity to typical glass manufacturing plants.

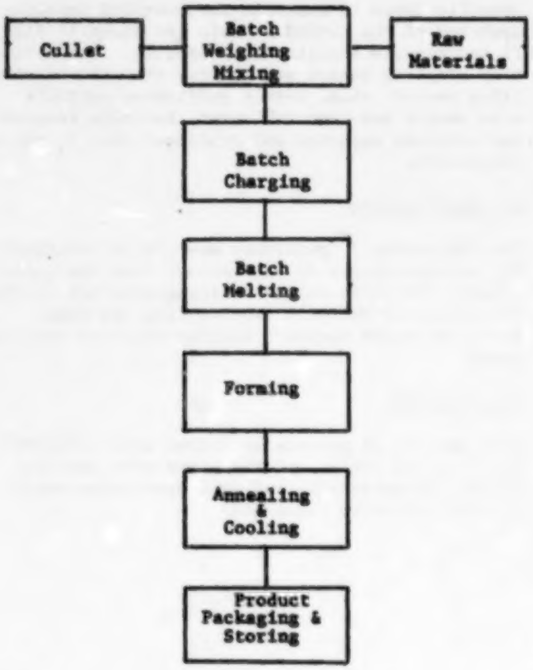

Figure 1 - Process Flow Diagram for Glass Manufacturing

The division among plant glass types include six producing container glass, two producing pressed and blown, and one flat glass. Wherever possible, the tests were conducted using both oil firing and gas firing. Similarly, wherever possible, variations in batch composition were tested.

The test program strategy was designed to utilize those procedures which were most likely to be used by the EPA regulatory function or by industry when evaluating glass emissions in future programs. Thus, wherever possible, standard procedures were mandated to be used. In this manner, it was believed that close correlation between past and future testing programs would be maintained or at least inconsistencies would be apparent. This latter aspect of the test program was important since two different contractors were selected to perform the various tests. Scott Environmental Services was selected to conduct testing at five of the selected sites and Battelle at four sites.

Emission Sampling and Analysis

The emission sampling and analysis plan was selected to provide data to fill in gaps in the data available from the literature and from past emission measurement programs. Because much was already known about glass plants, and because of limitations on the effort available to this program, it was determined that the comprehensive emission measurement program characterized by the Level 1 SASS train measurements[3] could not be employed. Hence, specific procedures were selected to measure emissions thought to be of importance. Although all emissions were not measured at each plant, each of the following emissions was measured at one or more glass plants:

- o Particulate Mass
- o Fluorides
- o Trace Metals
- o Particle Size
- o SO_2 and SO_3
- o NO_x
- o CO, H_2S, COS, CS_2, and low-molecular-weight hydrocarbons
- o Organics

Sampling and Analysis Procedures

Particulate Sampling

The EPA Method 5 particulate sampling train[4] (including back half or impinger portion) was used as a guide for particulate sampling at the glass plants. A minimum filter temperature of 225 F was maintained. To reduce background values for trace metals analysis, Battelle selected tissue quartz filters and Scott selected acid-washed fiberglas filters.

Time integrated gas samples were taken during the particulate runs to determine the CO_2 and O_2 concentrations and thus, molecular weight of the stack gas needed for particulate emissions calculations. Analysis by Fyrite was completed at the end of each run.

The required Method 5 cleanup and analytical procedures were followed to determine mass particulate emissions. Particulate samples were desiccated for 24 hours and weights determined by measurements conducted in a constant temperature/constant humidity room.

Fluoride Sampling and Analysis

For glass plants using fluoride flux in the glassmaking process, separate runs were made to determine fluoride emissions. The fluoride sampling procedure used was that of EPA Method 13b.[5] Method 13b utilizes the Method 5 sampling train and procedures, except that CaO is added to the water and wash solutions before solvent evaporation to prevent loss of fluoride during evaporation.

Instead of using the specific ion electrode of Method 13b to determine fluoride content of the samples, Battelle utilized the distillation method of Willard Winkle[6] and determined the fluoride by ion chromatography.

Trace Metals Analysis

Various samples from the EPA Method 5 particulate sampling train were analyzed for trace metals by optical emission spectroscopy. Separate analyses were made for front-half wash, filter, and back-half wash.

Particle Size Measurements

The Anderson in-stack impactor was used for particle size measurements. To facilitate the gravimetric determinations, a light-weight fiberglas impaction substrate was placed on each impaction plate. The substrate material was preweighed to the nearest microgram in a constant temperature/constant humidity environment. A backup filter was placed at the outlet of the impactor to catch any material passing through the last impactor stage.

The standard EPA Method 5 operating nomograph was used to determine the appropriate nozzle diameters and Δp's for isokinetic sampling with the impactor.

After assembling the impactor, the sampling tip was plugged and the impactor was placed in the stack for a sufficient time to equilibrate to stack temperature. After approximately 10 to 15 minutes, the impactor was removed from the stack, the nozzle plug was removed from the nozzle, the impactor nozzle was reinserted into the stack and placed at a preselected sample point and sampling commenced. Isokinetic sampling was conducted at one or more sampling points. The sampling rate through the nozzle and impactor was maintained at a constant flow rate, as determined from the nomograph.

A sampling time was selected to collect a sufficiently representative mass for gravimetric analysis. At the end of a predetermined time, the sample flow was stopped, the impactor was removed from the stack and the impactor flow terminated simultaneously. The impactor was taken to an onsite mobile laboratory and disassembled. The special light-weight substrates from each stage and the backup filter were placed in individual containers for storage until mass determinations could be made at the laboratory. The impactor was allowed to cool and then the nozzle and all surfaces upstream of the first impaction plate were washed with reagent grade acetone to remove any relatively large material impacted in the nozzle or adhered to the impactor surface. The impactor was then reassembled and testing was resumed. All gravimetric determinations for gross and tare weights were performed in a constant temperature/constant humidity laboratory.

SO_2 and SO_3 Measurements

The EPA Method 8 sampling train[7] was used for SO_2 and SO_3 determinations.

Scott chose to conduct separate runs for SO_2 determinations and particle size measurements. Battelle chose to assemble the Anderson impactor upstream of the Method 8 train (as shown in Figure 2) and conduct simultaneous sampling. The particle size sampling period was shorter than the SO_2 sampling period; thus, when a sufficient particle size sample had been collected, Battelle removed the Anderson impactor and continued the SO_2 run to completion.

NO_x Measurements

The EPA Method 7[8] procedure was used to measure NO_x concentrations in the exhaust from the glass plants. Battelle collected integrated bag samples and collected Method 7 samples from the bags; Scott collected Method 7 samples directly from the stack.

Gas Analysis

Grab samples of gaseous emissions were collected in 3-l glass flasks and the gases were analyzed by gas chromatography and mass spectrophotometry for the following compounds:

- o CO_2
- o O_2
- o AR
- o N_2
- o CO
- o SO_2
- o H_2S
- o COS
- o CS_2
- o H_2
- o CH_4
- o C_2H_6
- o C_3H_8
- o Iso-C_3H_8
- o n-C_4H_{10}
- o Iso-C_4H_{10}

Organic Sampling and Analysis

Where emissions from the glass forming area are vented to the atmosphere via large hoods, it was determined that organic emissions in the hood exhaust should be determined. To determine the organic constituents produced in the forming area, a Tenax column was used to collect samples for organic analyses. A schematic drawing of the organic sample train (with appropriate pumps and metering apparatus) is given in Figure 3.

Organic samples were fractionated using the liquid chromatography/infrared spectroscopy procedure, as incorporated in Level 1 Source Assessment Analysis procedures. Gravimetric-determinations of each fraction were made, and the primary compounds or type of compounds in each fraction were identified.

Problems Encountered in Sampling and Analysis

Because nearly all the sampling and analysis procedures utilized in this program were established methods, few unique problems were encountered. The only troublesome problem encountered was irregular flow profiles when sampling just upstream of the Morgan ejectors utilized at some plants. The problem of obtaining a representative sample at the poor sampling location available was overcome by using a large number (48) of sampling points.

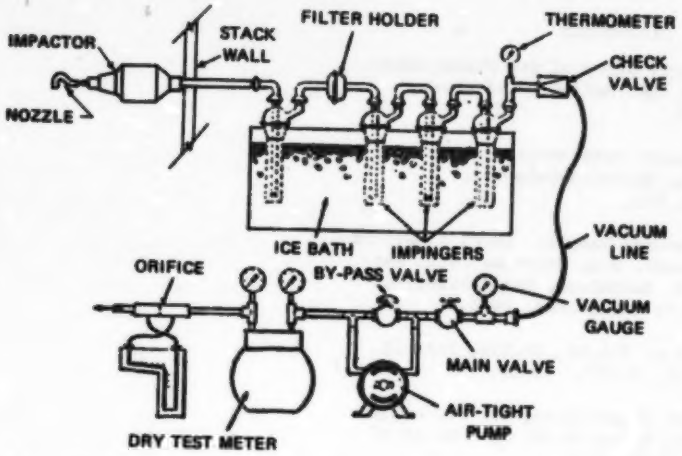
IMPACTOR
NOZZLE
STACK WALL
FILTER HOLDER
THERMOMETER
CHECK VALVE
ICE BATH
IMPINGERS
VACUUM LINE
ORIFICE
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
AIR-TIGHT PUMP
DRY TEST METER

FIGURE 2. MODIFIED EPA METHOD 8 SAMPLING TRAIN CONFIGURATION FOR USE IN COMBINED PARTICLE SIZE AND SO_x SAMPLING

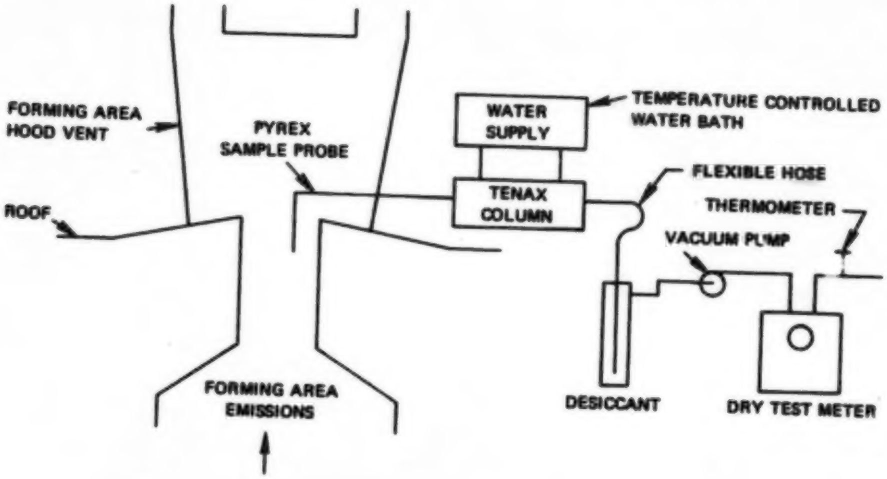
FORMING AREA HOOD VENT
PYREX SAMPLE PROBE
WATER SUPPLY
TEMPERATURE CONTROLLED WATER BATH
TENAX COLUMN
FLEXIBLE HOSE
THERMOMETER
ROOF
VACUUM PUMP
DESICCANT
DRY TEST METER
FORMING AREA EMISSIONS

FIGURE 3. SAMPLE TRAIN CONFIGURATION FOR SAMPLING ORGANIC EMISSIONS FROM GLASS FORMING AREA

The process emissions measured at one glass plant were sampled from a natural draft stack having gas temperatures of approximately 850 F. Because of the relatively high gas temperatures, a stainless steel probe liner was used in place of the glass liner. For these runs it was observed that the Viton seals (which are used to prevent air leakage where the nozzle connects to the probe) became brittle due to the heat; thus, they were replaced after each run.

For sampling runs where it was determined to use more than one sampling point for obtaining particle size data, it was necessary to change nozzles between traverse points. The flow through the impactor had to remain constant to maintain the cutoff sizes for the various impactor stages. Thus, when maintaining isokinetic sampling while moving from one sampling point to another with a different gas velocity, it was required that the sampling nozzle size be changed rather than altering the sampling rate.

References

1. Industrial Energy Study of the Glass Industry to FEA and DOC, Battelle-Columbus, Dec 1974, P-10.

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3. IERL-RTP Procedures Manual: Level 1 Environmental Assessment, J.W. Hamersma, S.L. Reynolds, and R.R. Maddalone, EPA Publication No. EPA-600/2-76-160a, June, 1976.

4. Federal Register, Vol.36, No.159, Part II, August 17, 1971, P-15713-15717.

5. Code of Federal Regulations, 40, Protection of Environment, Parts 60-99, Revised as of July 1, 1976, P-110-117.

6. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 13th Edition, 1971, P-171-172.

7. Op. cit. (5), P-85-88.

8. Op. cit. (5), P-82-85.

COMPREHENSIVE ANALYSIS OF EMISSIONS FROM FLUIDIZED-BED COMBUSTION PROCESSES

by

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Abstract

Results of the comprehensive analysis of emissions from a pressurized fluidized-bed combustion unit (the Exxon Miniplant) are described as an illustration of the methodology for comprehensive analysis. The results are discussed in the context of the overall environmental assessment of the process being conducted by the United States Environmental Protection Agency. The comprehensive analysis of the fluidized-bed combustion emissions and process streams involved approximately 740 measurements on about 90 samples, using more than 40 different inorganic, organic, and physical analytical methods. A discussion is presented covering the methods used for sample preparation, inorganic analysis, organic analysis, and physical measurements. The quality control procedures, and the accuracy of the estimates derived from the data are discussed.

Introduction

Environmental data acquisition is one of the seven major steps (Figure 1) in conducting a complete environmental assessment of new energy technologies such as fluidized-bed combustion of coal (Reference 1). The primary means for this data acquisition is comprehensive analysis of emissions. Precommercial stage comprehensive analysis (CA) of emissions from FBC units provides the opportunity to detect potential environmental problems early in the development of the process. The environmental assessment of the process based on the CA data should assist in the identification and/or development of most cost-effective control technologies that may be required.

A phased approach in three levels is the currently accepted technique for sampling and analyzing emissions. The three levels of analysis are defined as follows:

- Level 1 analysis is devised for comprehensive screening of a wide variety of organic and inorganic components. Level 1 sampling and analysis is designed to rapidly identify the potential pollutants from a source, and to measure them with a target accuracy factor of ±3. It also identifies all process streams that may contain four types of pollutants: gaseous, particulates, liquids/slurry, and solids. Level 1

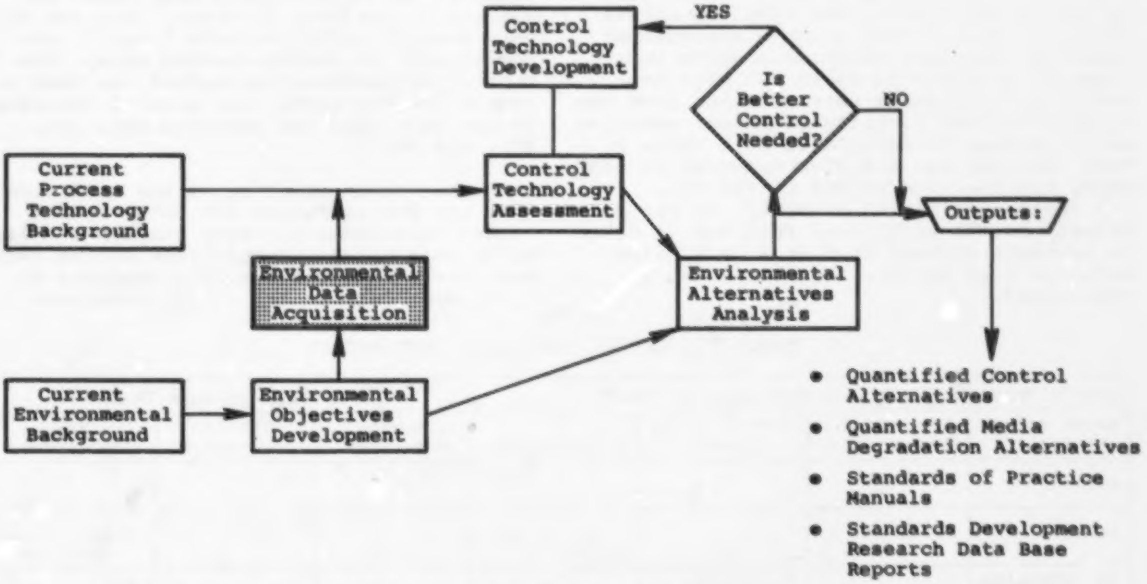
Control Technology Development
YES
Is Better Control Needed?
NO
Current Process Technology Background
Control Technology Assessment
Outputs:
Environmental Data Acquisition
Environmental Alternatives Analysis
Current Environmental Background
Environmental Objectives Development
• Quantified Control Alternatives
• Quantified Media Degradation Alternatives
• Standards of Practice Manuals
• Standards Development Research Data Base Reports

Figure 1. Simplified block diagram of environmental assessment steps.

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*Exxon Research & Engineering Company, Linden NJ 07036.

strategy also includes bioassay testing of several effluent streams to obtain a direct index or estimate of their toxicity potential.

- Level 2 analysis is based on Level 1 results. More accurate, compound-specific analytical techniques are used to pinpoint problem pollutants and effluent streams. The Level 1 data together with bioassay data and multimedia environmental goals will be used to identify Level 2 and 3 analytical needs.
- Level 3 analysis (not yet defined completely), would include routine continuous monitoring of those pollutants identified as specific problems in Level 2.

A set of twelve biological tests was used in Level 1 testing. These tests and the samples on which they were used are given in Table 1. They are designed to test the possible toxicity of a waste stream to mammalian, marine, freshwater, plant, and soil systems. This test protocol provides a fairly good representation of the various biological constituents of the environment that might be exposed to a waste stream. The bioassays are designed to be implemented quickly and inexpensively, in keeping with the screening nature of Level 1 testing. Their output will permit a relative ranking of waste streams according to biological hazard, and, together with the chemical and physical data, will provide an overall hazard characterization of the waste streams.

The measurement techniques and results presented in this paper are based largely on Level 1 analysis. The sampling matrix for Level 1 (and some Level 2 analysis of substances already known as problem pollutants) is shown in Table 2. Data presented in this paper were obtained from the pressurized FBC facility at Exxon; sampling was conducted in accordance with Table 2. This facility has a 0.32-m-diameter reactor which was operated at 890 C, 900 kPa, 1.2 m/sec superficial velocity, 40 percent excess air, 75 kg/hr coal feed and 11.0 kg/hr dolomite sorbent feed at a Ca/S molar ratio of 1.25 for the tests reported in this paper.

Sampling Methods, Analytical Techniques, and Quality Control Procedures

Sampling Methods

The comprehensive analysis program for the EXXON unit consisted of sampling seven of the nine streams shown in Figure 2. The nine streams are (1) coal feed, (2) dolomite feed, (3) 2nd stage cyclone discard, (4) bed reject material, (5) cyclone discard leachates, (6) bed reject material leachates, (7) undiluted stack gas, (8) diluted stack gas, and (9) dilution and combustion air. Sampling of the sorbent regenerator unit was not performed since this unit was not operated during the tests. Streams (5) and (6) were simulated in the laboratory since no leachate streams were actually present at the miniplant site.

Five tests were conducted at EXXON over the period of March 28 to April 1, 1977, during which the Miniplant was operated continuously for about 80 hours. Sampling was performed on an around-the-clock basis by two 7-man teams working 12 hour shifts. During each test, lasting five hours, the various FBC streams were sampled by the techniques given in Table 2 and elaborated in Table 3.

Grab samples of solids from the FBC process streams were taken periodically throughout each test. The individual samples were composited to obtained one sample per test. The gases (CO, CO_2, O_2, SO_2, etc.) in the undiluted flue gas at (7) were sampled continuously for analyses by the EXXON on-line instrumentation. Integrated bag samples were also taken for CO_2 and O_2 analyses by Orsat. SO_2 and NO_x were sampled by EPA Methods 6 and 7, respectively, to provide backup data. The controlled condensation method was used to sample for SO_3/H_2SO_4, and special impinger trains were used for sampling NH_3, HCN, HCl, and HF.

Continuous sampling of the undiluted flue gas was performed for total hydrocarbon measurements. Grab samples in glass bulbs were taken several times during each test for gas chromatographic analysis of C_1-C_6 hydrocarbons and sulfur compounds.

TABLE 1. LEVEL 1 BIOASSAY TEST MATRIX

Sample Type	Health Effects Tests			Ecology Effects Tests		
Water and Liquids	Microbial Mutagenesis	Rodent Acute Toxicity	Cytotoxicity	Algal Bioassays	Static Bioassays	Soil Microcosm
Solids	■	■	■	■	■	■
Gases						Plant Stress Ethylene
Particulates	■		■			Soil Microcosm
Sorbent	■		■			

TABLE 2. SAMPLING AND ANALYSES TO BE PERFORMED IN COMPREHENSIVE ANALYSIS OF FBC UNITS

			System Stream or Material								
			Stack			Solid Waste					
			Particulates			Collection				Leachate from Solid Waste	
Species, Pollutants	Sample Collection Technique(a)	Analysis Method(b)	Mid >3μ	Fine <3μ	Gas	Device Discard	Bed Reject	Coal Feed	Sorbent Feed	Collection Device	Bed
CONTINUOUS GAS MEASUREMENTS											
CO_2	Cw	NDIR(c)			X						
CO	Cw	IR or UV(c)			X						
NO	Cw	CL(c)			X						
NO_2	Cw	CL(c)			X						
SO_2	Cw	NDIR(c)			X						
O_2	Cw	PM(c)			X						
INTEGRATED GAS MEASUREMENTS											
CO_2	IG	FGC/TC			X						
CO	IG	FGC/TC			X						
NO_x	IG + M7	FGC/TC + M7			X						
SO_2	IG + M6	FGC/TC + M6			X						
O_2	IG	FGC/TC			X						
N_2	IG	FGC/TC			X						
H_2O	IG	FGC/TC			X						
H_2S	IG	FGC/FPD			X						
COS	IG	FGC/FPD			X						
$CH_3SH - C_6H_{13}SH$	IG	FGC/FPD			X						
$C_1 - C_6$ hydrocarbons	IG	FGC/FID			X						
$C_1 - C_{12}$ hydrocarbons	IG	FGC/FID			X						
$C_1 - C_6$ chlorocarbons	IG	FGC/EC			X						
NH_3	IG	FGC/TC			X						
HCN	IG	FGC/TC			X						
Cyanogen	IG	FGC/TC			X						
SO_3/H_2SO_4	GR/St	Ion chromatograph			X						
HCl	St	Titration			X						
Fluoride	St	SIE			X						
INTEGRATED SPECIMENS FOR SUBSEQUENT GROUP ANALYSIS											
Inorganic Chemicals											
71 elements (Li through U)	SASS/GS	SSMS	X	X		X	X	X	X	X	X
Proximate (fuels)	Gs	ASTM D3172-73						X			
Ultimate	Gs	ASTM D3176-74	X	X				X			
Sulfur forms (fuels)	Gs	ASTM D2492-68						X			
Radionuclides (Gross α & β)	SASS/Gs	LBPC	X	X		X	X	X	X		
Organic Chemicals											
Organics by class	SASS/Gs	LC/IR (total sample and 8 fractions)	X	X	X	X	X	X			
Organic compounds	SASS/Gs	LC/LRMS (selected fractions)	X	X	X	X	X	X			
POM	SASS/Gs	GC/MS	X	X	X	X	X	X			
Organic – reduced sulfur compounds	SASS/Gs	GC/FPD (8 fractions combined)	X	X	X	X	X	X			
C_7–C_{12} hydrocarbons	SASS/Gs	GC/FID	X	X	X	X	X	X			
Organic mass	SASS/Gs	Microbalance (8 fractions)	X	X	X	X	X	X			

INTEGRATED SPECIMENS FOR SUBSEQUENT SPECIFIC ANALYSIS											
Volatile, toxic elements											
(Be, Cd, Hg, Pb, Se, Sb, Te)	SASS/Gs	AAS	X	X	X	X	X	X	X	X	X
As	SASS/Gs	Colorimetric	X	X	X	X	X	X	X	X	X
Cl^-	SASS/Gs	Colorimetric	X	X						X	X
F^-	SASS/Gs	Distillation/colorimetric	X	X		X	X			X	X
Na	Gs	AAS						X			
Ca	Gs	AAS/titration						X	X		
Mg	Gs	AAS							X		
$CO_3^=$	SASS/Gs	Gas evolution	X	X		X	X	X	X		
$SO_4^=$	SASS/Gs	Titration/Ion chromatography	X	X		X	X	X	X	X	X
$SO_3^=$	SASS/Gs	SO_2 evolution/colorimetric	X	X		X	X	X	X	X	X
$S^=$	SASS/Gs	H_2S evolution/titrations	X	X		X	X	X	X		
NO_2^-	SASS/Gs	Colorimetric	X	X		X	X	X	X	X	X
NO_3^-	SASS/Gs	Colorimetric	X	X		X	X	X	X	X	X
C (non-carbonate)	Gs	Combustion				X	X	X	X		
Heating value	Gs	ASTM D 2015-66						X			
Particle morphology	Gs	LM/SEM				X	X	X	X		
Particle size	Gs	Sieve ASTM D 410-38				X	X	X	X		
Particle mass	SASS/M5	Weight	X[d]	X							
BIOLOGICAL ASSAYS											
Health											
Microbial mutagenesis	SASS/Gs	Salmonella/Ames	X	X	X	X	X	X	X		X
Cytotoxicity	SASS/Gs	Human lung fibroblast (WI-38)			X						X
Cytotoxicity	SASS/Gs	Rabbit alveolar macrophage (RAM)	X	X		X	X	X	X		
Acute toxicity	SASS/Gs	In vivo rodent				X	X	X	X		X
Ecological											
Freshwater algal	SASS/Gs	Algal bottle				X	X	X	X	X	X
Freshwater animal (daphnia)	SASS/Gs	Static				X	X	X	X	X	X
Freshwater animal (fish)	SASS/Gs	Static				X	X	X	X	X	X
Saltwater algal	SASS/Gs	Unicellular marine algae				X	X	X	X	X	X
Saltwater animal (grass shrimp)	SASS/Gs	Static				X	X	X	X	X	X
Saltwater animal (fish)	SASS/Gs	Static				X	X	X	X	X	X
Terrestrial soil	SASS/Gs	Soil microcosm	X	X		X	X	X	X	X	X
Terrestrial plant	SASS/Gs	Stress ethylene			X						

Reference Legend

(a) Cw – Continuous withdrawal through nonreactive line with mechanical filtration
IG – Integrated grab sample of gas in glass bulb
GR/St – Gokssyr-Ross coil/special sampling train
St – Separate wet chemical train to collect gas (such as Method 6)
SASS – Source Assessment Sampling System (train used for suspended particulates, organics, and volatile trace elements)
Gs – Grab multiple samples riffled to reduce to 100 g representative sample
M5 – EPA Method 5
M6 – EPA Method 6
M7 – EPA Method 7.
(b) NDIR – Nondispersive infrared
IR – Infrared
UV – Ultraviolet
CL – Chemiluminescence
PM – Paramagnetic
FGC/TC – Field Chromatograph/thermal conductivity detector
FGC/FPD – Field Chromatograph/flame photometric detector
FGC/FID – Field Chromatograph/flame ionization detector
FGC/EC – Field Chromatograph/electron capture detector
SIE – Selective-Ion Electrode
SSMS – Spark Source Mass Spectroscopy
ASTM – American Society for Testing Materials Standard Method
LBPC – Low background gas proportional controller
LC – Liquid Chromatography
LRMS – Low Resolution Mass Spectrometry
GC – Gas Chromatography
GC/MS – Gas Chromatography with Mass Spectrography
AAS – Atomic Absorption/Spectroscopy
LM/SEM – Light Microscopy/Scanning Electron Microscope.

(c) Or acceptable instrumentation already installed at FBC Unit.

(d) Coarse (>10 μ) and Filter (<1 μ) fractions included.

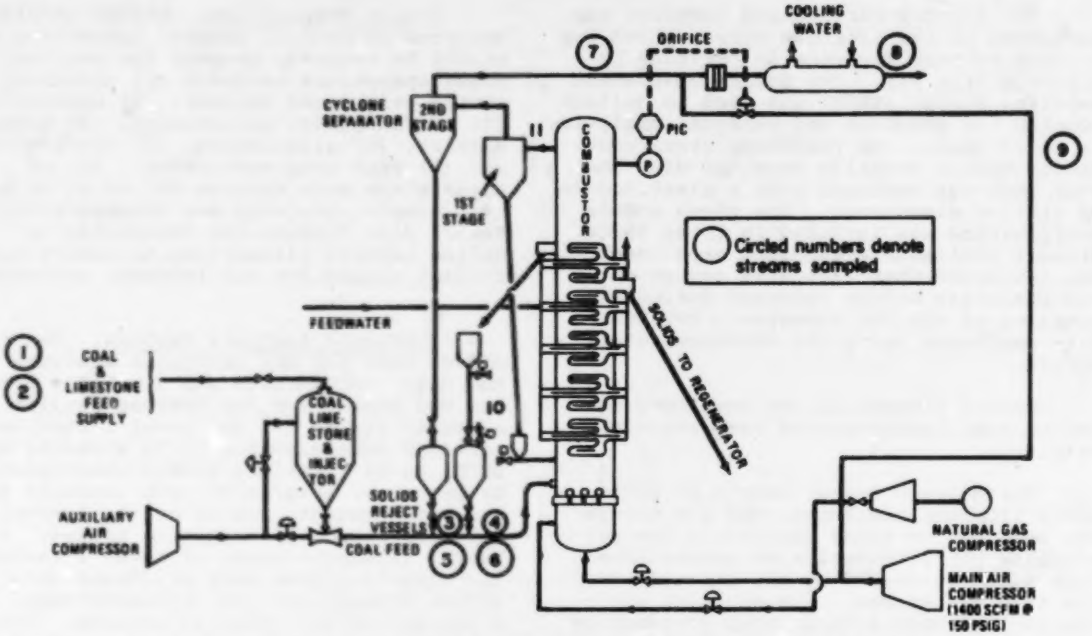
COOLING WATER
ORIFICE
⑦
⑧
CYCLONE SEPARATOR
2ND STAGE
11
COMBUSTOR
PIC
P
⑨
1ST STAGE
Circled numbers denote streams sampled
FEEDWATER
SOLIDS TO REGENERATOR
①
②
COAL & LIMESTONE FEED SUPPLY
COAL LIME-STONE & INJECTOR
10
SOLIDS REJECT VESSELS
③
④
AUXILIARY AIR COMPRESSOR
COAL FEED
⑤
⑥
NATURAL GAS COMPRESSOR
MAIN AIR COMPRESSOR (1400 SCFM @ 150 PSIG)

Figure 2. The fluidized-bed combustion miniplant at EXXON during comprehensive analysis tests.

TABLE 3. SAMPLING TECHNIQUES USED FOR EXXON CA

Stream	Substance	Sampling Method(s)
Coal feed ①	Solid samples	Multiple grab
Dolomite feed ②		
2nd stage cyclone solids ③		
Bed reject ④		
Leachate from cyclone solids ⑤	Inorganics, organics	720-hr shake test
Bed reject leachates ⑥	Inorganics, organics	720-hr shake test
Flue gas, undiluted ⑦	CO	Continuous
	CO_2	Continuous and integrated bag
	O_2	Continuous and integrated bag
	NO	Continuous and Method 7 (NO_x)
	NO_2	Continuous
	SO_2	Continuous and Method 6
	Hydrocarbons	Continuous and grab, glass bulb
	Sulfur compounds	Grab, glass bulb
	SO_3/H_2SO_4	Condensation coil
	NH_3	Impingers, H_2SO_4
	HCN	Impingers, KOH
	HCl	Impingers, NaOH
	HF	Impingers, NaOH
	Particulates	Balston filter (heated)
Flue gas, diluted ⑧	Particulates	SASS and Method 5
Combustion and dilution air ⑨	Organics	Tenax trap

The primary particulate sampling was performed in the flue gas stream which was reduced to near atmospheric pressure by dilution with air. The Source Assessment Sampling System (SASS) was used to collect samples for chemical and physical analysis. In three tests, the stainless steel condenser module normally supplied with the SASS unit was replaced with a glass module of similar dimensions. The glass module modification was included in these tests since a preliminary sampling experiment had indicated that excessive corrosion of the stainless module occurred during the sampling of the FBC emission. Two tests were performed using the stainless steel module.

Method 5 sampling was performed to obtain compliance-related mass emission data.

The Balston filter sample of particulates from the undiluted flue gas stream was obtained to study changes in the particulate characteristics or composition that might be caused by the dilution of the flue gas stream. The dilution air was sampled with a Tenax trap to identify any organics that might contaminate the flue gas stream.

Analytical Procedures

Analyses were performed on samples from three of the EXXON sampling tests. Approximately 90 samples from the three tests were analyzed using more than 40 different inorganic, organic, and physical measurement methods. The analytical work was initiated about 1-1/2 weeks after the sampling, and was completed in about 2-1/2 months. The initial 1-1/2 week period was required to prepare samples for analysis.

Sample Preparation. Before laboratory analyses commenced, several operations were needed to properly prepare the samples. These operations included (1) obtaining sample weight and volumes, (2) compositing, (3) riffling, (4) pulverizing, (5) homogenizing, (6) aliquotting, (7) extractions, and (8) Parr bomb combustion. All of these steps were carried out so as to maintain sample integrity and representativity. Sample size limitations frequently required careful aliquotting to assure sufficient sample for all intended analyses.

Inorganic Analysis Methods. The techniques used for the inorganic analyses of the SASS, FBC process and leachates from the bed reject and 2nd cyclone samples are shown in Figure 3. The Level 1 analyses included determination of 71 elements by SSMS, Hg by flameless atomic absorption, Sb by atomic absorption with graphite furnace atomization, and As by the diethyl dithiocarbamate colorimetric method. A rather extensive group of Level 2 cation and anion analyses were performed using atomic absorption, ion chromatography, and a variety of wet chemical methods. Coal samples were analyzed by ASTM standard methods.

Organic Analyses. The organic analyses included the Level 1 and 2 determinations shown in Figure 4. Initially samples were Soxhlet extracted with methylene chloride; pentane was used for the extraction from the XAD-2 sorbent. The subsequent Level 1 analyses included: determination of the weight of organics in the sample, identification of organic classes by Fourier Transform Infrared Spectroscopy (FTIR) in both the unseparated extract sample and the eight

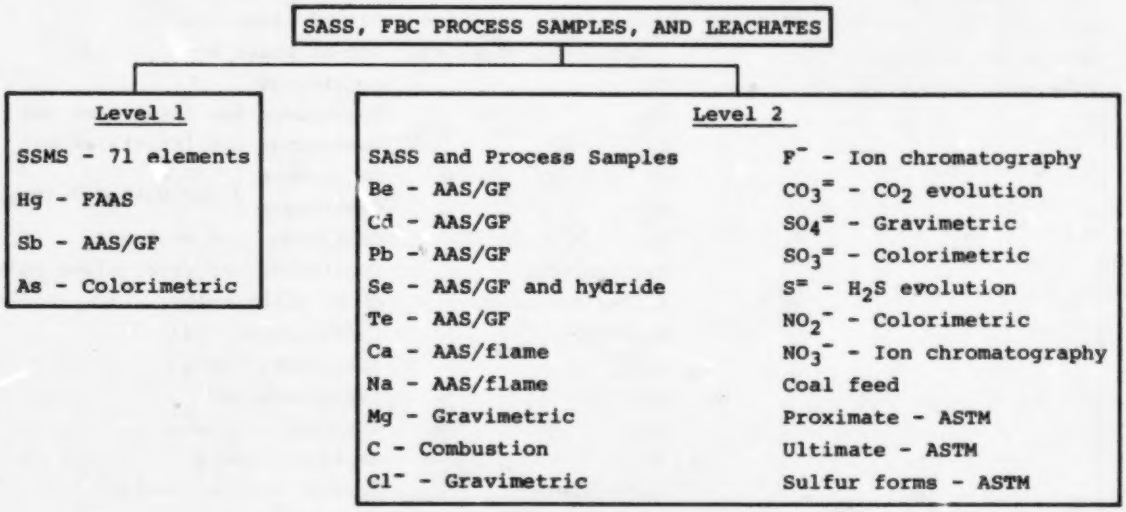
SASS, FBC PROCESS SAMPLES, AND LEACHATES
Level 1
SSMS - 71 elements
Hg - FAAS
Sb - AAS/GF
As - Colorimetric
Level 2
SASS and Process Samples
Be - AAS/GF
Cd - AAS/GF
Pb - AAS/GF
Se - AAS/GF and hydride
Te - AAS/GF
Ca - AAS/flame
Na - AAS/flame
Mg - Gravimetric
C - Combustion
Cl^- - Gravimetric
F^- - Ion chromatography
$CO_3^=$ - CO_2 evolution
$SO_4^=$ - Gravimetric
$SO_3^=$ - Colorimetric
$S^=$ - H_2S evolution
NO_2^- - Colorimetric
NO_3^- - Ion chromatography
Coal feed
Proximate - ASTM
Ultimate - ASTM
Sulfur forms - ASTM

Figure 3. Inorganic analysis performed in EXXON CA Program.

fractions derived by liquid chromatographic separation, determination of C_7-C_{12} hydrocarbons by gas chromatography with flame ionization detection (GC/FID), and examination of selected liquid chromatographic fractions by low resolution mass spectrometry (LRMS).

The Level 2 effort consisted of analyses for specific polycyclic organic matter (POM) compounds by combined gas chromatograph/mass spectroscopy (GC/MS) and determination of specific organic sulfur compounds in the samples by gas chromatography with flame photometric detection (GC/FPD).

Physical Measurements. The physical measurements outlined in Figure 5 were performed on all SASS and FBC stream solid samples. Normal light and polarized light microscopy at magnifications of 10 to 250X were used to obtain data on the shape, structure, cleavage, color, and particle size distribution in the various samples. Scanning electron microscopy (SEM) was used to examine the finer particles collected in the SASS cyclones and on the SASS filter.

Radioactivity measurements for gross alpha and beta emissions were performed by counting a portion of each sample in a Beckman low-background proportional counter.

Quality Control Procedures

Several techniques were used to assess the quality of the EXXON inorganic analytical data. These included:

1. The analysis of NBS Standard Reference Materials (SRM)
2. Dynamic spiking techniques
3. Comparison of results obtained by two different analytical methods, spark source mass spectroscopy (SSMS) and atomic absorption spectrometry (AAS).

The NBS samples used in this work were SRM 1631B (coal), SRM 1632 (coal), SRM 1633 (coal fly ash) and SRM 88a (dolomite). The matrices of these standards are quite similar to the FBC feedstocks and emission stream samples. Reference values are available for over 40 elements in the SRM 1632 coal and SRM 1633 fly ash, and certified values for 11 elements in the SRM 88a dolomite are given. SRM 1631B coal is certified by NBS for ash and sulfur content.

SSMS analyses were performed on SRM's 1632, 1633, and 88a. In these and other analyses involving the standards, the materials were submitted as blind samples without the analyst being informed that standards were included along with the series

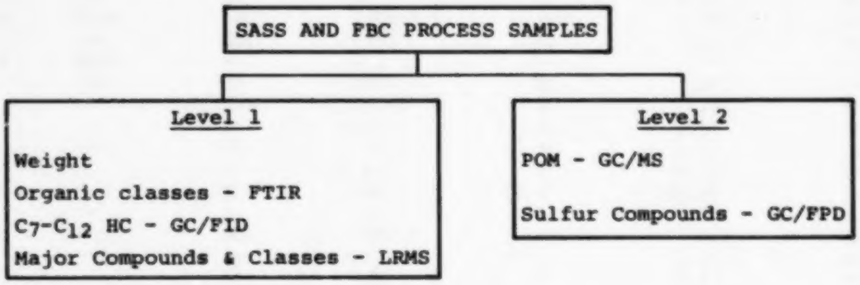
SASS AND FBC PROCESS SAMPLES
Level 1
Weight
Organic classes - FTIR
C_7-C_{12} HC - GC/FID
Major Compounds & Classes - LRMS
Level 2
POM - GC/MS
Sulfur Compounds - GC/FPD

Figure 4. Organic analysis performed in EXXON CA Program.

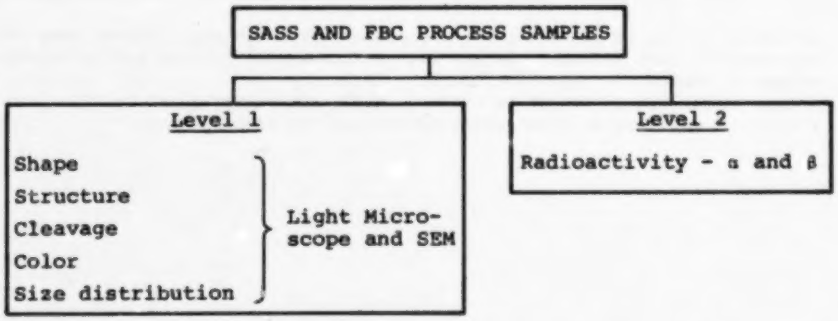
SASS AND FBC PROCESS SAMPLES
Level 1
Shape
Structure
Cleavage
Color
Size distribution
Light Microscope and SEM
Level 2
Radioactivity - α and β

Figure 5. Physical analysis performed in EXXON CA Program.

TABLE 4. SPARK SOURCE MASS SPECTROGRAPHIC ANALYSIS OF NBS STANDARD REFERENCE MATERIALS

Results in μg/g, except as indicated

	NBS SRM 1632 (Coal)		NBS SRM 1633 (Fly Ash)		NBS SRM 88a (Dolomite)[b]	
Element	Ref. Value[a]	BCL	Ref. Value[a]	BCL	Ref. Value	BCL
Al	1.9%	2.7%	12.5%	15%	0.19	0.3
As	(5.9)	7	(61)	40	—	—
Ba	405	670	2780	2000	—	—
Br	14.2	16	6.0	15	—	—
Ca	0.44%	1%	4.34%	3%	30.1	42
Cd	(0.19)	0.1	(1.45)	5	—	—
Ce	18.5	14	146	100	—	—
Cl	1000	640	42	40	—	—
Co	(6)	13	(38)	30	—	—
Cr	(20.2)	32	(131)	100	—	—
Cs	1.4	1	8.6	20	—	—
Cu	(18)	64	(128)	150	—	—
Eu	0.21	0.2	2.86	3	—	—
Fe	(0.87%)	2%	6.37%	10%	0.28	0.6
Ga	8.5	5	49	40	—	—
Hf	0.95	1	10.8	6	—	—
In	0.07	<0.1	—	—	—	—
Hg	(0.12)	<0.2	(0.14)	0.4	—	—
K	0.29%	0.24%	1.72%	1.5%	0.12	0.6
La	10.5	5	82	40	—	—
Mg	0.25%	0.38%	(1.98%)	2%	21.3	25
Mn	(40)	32	(493)	500	0.03	0.04
Mo	3.4	3	—	—	—	—
Na	390	280	(3070)	1000	0.01	0.004
Ni	(15)	14	(98)	100	—	—
P	—	—	—	—	0.01	0.004
Pb	(30)	32	(70)	40	—	—
Rb	24	38	(112)	200	—	—
Sb	3.9	7	6.9	2	—	—
Sc	4.5	1	32	30	—	—
Se	(2.9)	6	(9.4)	5	—	—
Si	(3.2%)	6.9%	21%	15%	1.2	1.1
Sm	1.7	1	15	5	—	—
Sr	144	160	(1380)	700	0.01	0.006
Ta	0.17	≤2[c]	1.6	≤0.6	—	—
Th	(3.0)	2	(24)	15	—	—
Ti	(800)	1000	6920	6000	0.02	0.01
U	(1.4)	1	(11.6)	8	—	—
V	(35)	16	(214)	200	—	—
Zn	(37)	70	(210)	200	—	—
Zr	45	6	301	200	—	—

(a) Reference values in parentheses are given by NBS. The other values were taken from work by ORNL and LLL. Reference: Environmental Science and Technology, Volume 9, Number 10, page 975 (October, 1975).

(b) Values in percent by weight as oxides. Reference values given by NBS.

(c) Possible contamination from source holder used in SSMS analysis.

of FBC samples. The results of the SSMS analyses are given in Table 4 along with the corresponding reference values given by NBS or derived from work by Lawrence Livermore Laboratory (LLL) and Oak Ridge National Laboratory (ORNL). A summary of the comparison of the SSMS values with the reference values is presented in Table 5, including the factor of 2 to 3 accuracy requirement for Level 1 analysis.

TABLE 5. SUMMARY OF COMPARISON OF SSMS VALUES WITH NBS STANDARD REFERENCE VALUES

SRM 1632 Coal (37 comparisons)[(a)]

27 elements differ by less than a factor of 2

7 elements differ by less than a factor of 3

1 element (Cu) differs by a factor of 3.6

1 element (Sc) differs by a factor of 4.5

1 element (Zr) differs by a factor of 7.5

SRM 1633 Fly Ash (35 comparisons)[(a)]

28 elements differ by less than a factor of 2

6 elements differ by a factor of 3 or less

1 element (Cd) differs by a factor of 3.5

SRM 88a Dolomite (11 comparisons)

8 elements differ by a factor of 2 or less

3 elements differ by less than a factor of 3

(a) Comparisons do not include As, Hg, or Sb.

Based on comparisons of SSMS results and reference values for 37 elements in the NBS coal samples, 73 percent of the measurements agree within a factor of 2, and 92 percent agree within a factor of 3. SSMS results for Cu, Sc, and Zr differed from the reference values by more than a factor of 3. Comparisons of 35 elements in the NBS fly ash show that 80 percent of the SSMS and reference values agree within a factor of 2, and 97 percent agree within a factor of 3. Only Cd differed slightly more than a factor of 3 with the reference value. For the dolomite (11 comparisons), 73 percent agree within a factor of 2 and SSMS values for all elements are within a factor of 3 of the reference values.

The NBS coal and fly ash samples were also analyzed for As, Be, Cd, Hg, Pb, Se, Sb, and Te by the Level 1 and Level 2 methods used for the FBC samples. The results of the analyses and the reference values are presented in Table 6. With exception of Se in the fly ash, all results are within the estimated uncertainties given by NBS and LLL.

The analyses of the NBS dolomite standard for Ca, Mg, and CO_2 and the 1631B coal standard for ash and total sulfur are given in Table 7. The analyses were performed by ASTM standard methods. Satisfactory agreement with certified values was obtained for each measurement.

Many samples in the EXXON work were analyzed both by SSMS and by AAS for Be, Cd, Pb, Se, and Te. Since AAS is an inherently accurate analytical method, comparison of the values obtained by the two methods provides another means to estimate the quality of the SSMS data. Table 8 presents a comparison of the SSMS and AAS values obtained for various sample types analyzed in the EXXON program. Based on a comparison of 21 samples for the 5 elements, 80 percent of the SSMS values were within a factor of 3 of the AAS results. The disagreement observed in the comparisons is mostly due to the low SSMS values for Be and the high values obtained for all elements except Pb in the acid condensate from the SASS condenser module.

In the analysis of the SASS impinger solutions and selected FBC samples by AAS, dynamic spiking was used to estimate the analytical accuracy. A summary of the spike recoveries for the various analyses is shown in Table 9.

Satisfactory spike recoveries were obtained for all element sample combinations which were analyzed by the AAS/graphite furnace and flameless AAS methods. Unacceptably low spike recoveries were obtained by analysis of the SASS impinger solutions using the AAS/hydride generation method. Therefore, Se analysis by the AAS/graphite furnace techniques was selected as the preferred method for these samples.

Summary and Conclusions on Sampling Methods, Analytical Techniques, and Quality Control Procedures

Based on experience gained to date in applying CA sampling and analysis procedures to fluidized bed combustors, the following comments and conclusion can be made on the efficacy of the methods.

Sampling Methods. In general, the sampling methods as used for the EXXON program performed satisfactorily. However, some problems were encountered in the use of the SASS train. Leakage around the filter was observed during the initial tests because the two filter body halves did not properly match to seal the filter

TABLE 6. ANALYSIS OF STANDARD REFERENCE MATERIALS

Results in μg/g

Element	BCL Analytical Method[(a)]	NBS/SRM 1632 (Coal) Ref. Value[(b)]	NBS/SRM 1632 (Coal) BCL	NBS/SRM 1633 (Fly Ash) Ref. Value[(b)]	NBS/SRM 1633 (Fly Ash) BCL
Be	AAS/GF	(1.5)	2.5	(12)	15
Cd	AAS/GF	(0.19 ± 0.03)	0.19	(1.45 ± 0.06)	1.4
Hg	FAAS	(0.12 ± 0.02)	0.10	(0.14 ± 0.01)	0.10
As	Color	(5.9 ± 0.6)	5.5	(61 ± 6)	56
Pb	AAS/GF	(30 ± 9)	31	(70 ± 4)	68
Se	AAS/HG	(2.9 ± 0.3)	2.6	(9.4 ± 0.5)	7.5
Sb	AAS/GF	3.9 ± 1.3	3.5	6.9 ± 0.6	7.0
Te	AAS/GF	(<0.1)	<0.2	(c)	<0.5

(a) AAS/GF - Atomic absorption spectrometry/graphite furnace atomization
AAS/HG - Atomic absorption spectrometry/hydride generation
FAAS - Flameless atomic absorption spectrometry
Color - Colorimetric (silver diethyldithiocarbamate).

(b) Reference values in parentheses are given by NBS. The other values were taken from work by LLL. Reference: Environmental Science and Technology, Volume 9, Number 10, page 975 (October 1975).

(c) Reference value not given.

TABLE 7. CHEMICAL ANALYSIS OF NBS DOLOMITE AND COAL STANDARDS[(b)]

Analysis	Ref. Value, percent	BCL Value, percent
Dolomite - NBS/SRM 88a		
CO_2	46.6	46.8
Ca as CaO	30.1	30.4
Mg as MgO	21.3	21.7
Coal - NBS/SRM 1631 B		
Ash	14.59	14.2
Sulfur	2.016	1.92

(a) Analyses performed by ASTM methods.

TABLE 8. COMPARISON OF SSMS WITH AAS FOR FOR SELECTED ELEMENTS

Sample Type	Comparison of SSMS with AAS[(a)] Be	Cd	Pb	Se	Te
Coal	L		H	H	
Sorbent					
Bed Reject	L		L		
2nd Cyclone	L				
SASS, 10,3 μ cyclone catch	L			L	
SASS, 1 μ cyclone + filter catch	L				
SASS, acid condensate	H	H		H	H

(a) H - SSMS higher than AAS by more than a factor of 3
L - SSMS lower than AAS by more than a factor of 3
No entry - SSMS within ± a factor of 3 of AAS.
Summary: 105 comparisons
80% within ± a factor of 3
10% SSMS more than factor of 3 above AAS
10% SSMS more than factor of 3 below AAS.

TABLE 9. SPIKE RECOVERIES FROM SASS IMPINGER SOLUTIONS AND SELECTED FBC PROCESS SAMPLES

Element	Analytical Method[a]	Spike Recovery, percent			
		H_2O_2 Sample No. 1074	$(NH_4)_2S_2O_8/AgNO_3$ Sample No. 1075	Dolomite Feed Sample No. 1303	Coal Feed Sample No. 1308
Be	AAS/GF	96	95	104	ND[b]
Cd	AAS/GF	104	106	99	99
Hg	FAAS	100	96	ND	100
Pb	AAS/GF	95	90	112	116
Sb	AAS/GF	96	92	ND	ND
Se	AAS/GF	95(70)[c]	100[d]	93	ND
Te	AAS/GF	95	95	90	95

(a) AAS/GF - Atomic absorption spectrometry/graphite furnace atomization
FAAS - Flameless atomic absorption spectrometry.

(b) ND - not determined.

(c) Recovery in parentheses obtained by hydride generation method using 2 ml of H_2O_2 impinger solution.

(d) Very low recovery obtained by hydride generation method.

perimeter. This problem was remedied in subsequent tests by using two filter discs. Checks prior to tests frequently showed leakage around the Teflon cyclone gaskets. Evidently the problem was caused because the Teflon gasket became distorted in the previous test and would not reseal properly. The use of new Teflon gaskets for each test minimized this problem. Design changes should be made to eliminate the filter and cyclone leakage problems.

An unresolved problem with regard to the SASS train is whether a glass or stainless steel condenser module should be used. In the EXXON sampling, rather severe corrosion of the stainless steel module was observed as a greenish deposit at the inlet from the filter. The deposit could not be effectively removed either by brushing or scraping during the cleanup operations and could not be collected quantitatively as desired.

Of more significance are the differences observed in the concentration of certain elements in the condensate collected in the glass and stainless modules. Based on AAS analysis, selenium concentrations were significantly higher (over 20X) in the glass module condensate. On the other hand, cadmium concentrations were significantly higher (about 15X) in the stainless module condensate. Significant differences were not observed in the concentrations of Be, Hg, As, Pb, Sb, and Te in the glass and stainless condensate solutions.

Additional studies may be conducted to determine the reasons for the differences in Se and Cd concentrations in the condensates from the glass and stainless condenser modules, and to decide which type should be used in future comprehensive analyses to obtain reliable trace element data. Till then, for FBC units, the glass module should be preferred because of its significantly reduced potential for corrosion and for contamination of samples.

Analytical Techniques. The quality control data obtained in the EXXON study demonstrates that SSMS can provide data within the required Level 1 accuracy. However, in order to minimize sample handling and related errors, and to reduce costs, it is suggested that the Parr bomb combustion step be eliminated when possible, i.e., when organics are not present in the samples. In the case of FBC sample analyses, this would include the SASS particulates, 2nd cyclone discard, bed reject, and sorbent.

Atomic absorption spectrometry has been shown to be a suitable method for Level 1 and Level 2 Hg and Sb analyses. The colorimetric method for As is acceptable for Level 1 and 2 analysis, although the use of AAS for this element is known to provide a more sensitive, lower cost method of analysis. AAS procedures are also shown to be acceptable for Level 2 analysis of Be, Cd, Pb, Se, and Te.

However, Se analysis of the SASS impinger solutions by the hydride generation method presents some problems. The selenium hydride cannot be quantitatively evolved from the impinger solutions. These problems may be overcome by first destroying the peroxide and precipitating the silver with hydrochloric acid. It is also anticipated that a similar problem would be encountered in the arsenic analysis of the SASS impinger solutions by the arsine generation method for either AAS or colorimetric determination.

Quality Control Procedures. In the EXXON work, procedures to assess data quality were applied primarily to the inorganic analysis. In future work, emphasis will also be placed on incorporation of quality assessment measures into the organic analysis scheme.

Inter-laboratory analyses of standards and process samples are also strongly suggested as a means to better evaluate and improve CA analytical methodology.

Comprehensive Analysis Results

Some qualifications to the data presented below should be noted:

(1) This is the first extensive analysis of emissions on a fluidized-bed unit.

(2) Steady-state conditions may not have been achieved during the CA tests since the sulfur content of the coal varied. This resulted in drastic tapering of the SO_2 concentrations in the flue gas.

(3) The regenerator was not operated during CA runs at the Miniplant.

However, since the data collection process was well monitored and controlled, the data are considered reliable.

Results and Evaluation

Comparisons to MATEs. To evaluate the significance of the measured concentration of substances in the effluent streams, the measured concentrations were compared to the MATE (Minimum Acute Toxicity Effluent) values (Reference 2).

MATEs are indicators of allowable concentrations of contaminants in the effluent stream, and provide a point of reference for control technology goals. MATEs cannot be used as absolute indicators of minimum toxicity since they are still in the developmental stage.

The procedures involved in developing MATE values can be found in Reference 2. MATEs are approximate concentrations of contaminants in air, water, or land effluents which may evoke minimal significant harmful responses to humans or the ecology, within 8 hours. In general, types of data chosen to provide the basis for MATEs include threshold limit values (TLV), NIOSH recommendations, lethal dose concentrations and other toxicity data, drinking water regulations, and water quality criteria. For a single substance, five specific MATE concentrations can be defined: two air MATEs and two water MATEs (one each based on health and ecology effects) and one land MATE (based on the lower water MATE).

Emissions in Flue Gas. Samples of the flue gas were collected at about 900 kPa pressure before air dilution, and analyzed. Table 10 shows flue gas composition measured with on-line instruments and wet chemistry tests.

TABLE 10. ANALYSIS OF FLUE GAS

Substances	Concentration $\mu g/m^3$ (ppm)	Air MATE $\mu g/m^3$	Measured by
CO	61,734(53)	55,000	On-line instruments
CO_2	24 x 10^6	9 x 10^6	
O_2	5.5%	None	
HC	2196(3.3)	None	
H_2SO_4 Mist + SO_3	2079(5)	1,000	Wet chemistry
SO_2	74,813(28)	13,000	
NH_3	501(0.6)	18,000	
CN	1.2	5,000	
F	10,120(13)		
Cl	54,824(33)	3,000	
NO_x as NO_2	148,442(70)	9,000	
As	<2	2	Atomic absorption
Be	<0.4	2	
Cd	0.1	8.2	
Hg	0.85	50	
Pb	<1.2	150	
Sb	<1.7	500	
Se	<1.4	10.8	
Te	<1.7	100	

The lowest concentrations of SO_2 and NO_x in the flue gas are respectively 28 ppm (0.18 lb/10^6 Btu) and 70 ppm (0.09 lb/10^6 Btu). These are very low in comparison with existing New Source Performance Standards for coal-fired steam generators: 1.2 lb/10^6 Btu for SO_2, and 0.7 lb/10^6 Btu for NO_x.

However, in comparison with the MATEs shown in Table 10, both SO_2 and NO_x are much higher in concentration than the MATEs allow. In fact, the SO_2 concentration in the flue gas is about 6 times the MATEs value, and the NO_x concentration is 16 times. This fact does not necessarily mean that SO_2 and NO_x are a problem; but it indicates that the MATEs are deliberately conservative.

The concentrations of all the eight volatile toxic elements were well below the MATEs. Incidentally, arsenic concentration measured by spark source mass spectrography was higher than the MATEs; but the colorimetric analysis, classed as a Level 2 technique, showed it to be less than the MATE value.

Concentrations of polycyclic organic matter in flue gas given in Table 11 are all lower than the air MATEs.

TABLE 11. ORGANIC COMPOUNDS IN FLUE GAS

Substances	Concentrations, ng/m^3	Air MATE, ng/m^3
Anthracene/phenanthrene	53	483,000
Methyl anthracenes	5	483,000
Fluoranthene	26	90 x 10^6
Pyrene	9	233 x 10^6
Methylpyrene/fluoranthene	1.0	No data
Benzo(c) phenanthrene	0.2	26.9 x 10^6
Chrysene/benz(a)anthracene	3.8	44,800
Benzo fluoranthenes	1.0	897,000
Benz(a)pyrene	0.5	20
HC > C_6-C_{12}, $\mu g/m^3$	1740	No data
HC > C_{12}, $\mu g/m^3$	58	No data

Suspended Particulates in Flue Gas. The particulate concentration in the flue gas, after passing through two conventional cyclones, but without the use of fine particulate control equipment, was about 1.2 gr/scf (1.9 lb/10^6 Btu) as compared to the EPA standard of 0.1 lb/10^6 Btu. However, if an appropriate third-stage particulate control device that removes over 96% of the particulates can be demonstrated, the EPA emissions standard would be met.

The physical properties of the suspended particulates in the flue gas may be of interest. The size distribution and morphology are:

<1 micron	7% wt.
1 to 3 microns	39% wt.
3 to 10 microns	21% wt.
>10 microns	33% wt.

Predominant shape:	Irregular
Evident cleavage:	None
Structure:	3 phase
Color:	White, black, red

Thus, 46 wt. percent of the suspended particulates collected by the source assessment sampling system's cyclone (Reference 3) were less than 3 microns, and are in the respirable range. The α radioactivity averaged about 6 ± 3 pCi/g, and the β radioactivity, 30 ± 10 pCi/g.

Table 12 indicates that the toxic and volatile metal content in the particulates is of real significance. Since most of these particulates will be collected as solid wastes by any effective particulate collection system, the land MATE values apply. Of these metals, all but Te and Hg would exceed the land MATE even if the particulates were removed from the flue gas at a reasonable collection efficiency and were considered for land disposal (see Table 12). The second "Yes" in the MATE comparison column indicates that the particulates would still constitute a land disposal problem even when diluted by a factor of 100 by mixing with nontoxic materials (or some other technique) to reduce the toxic metal concentration. These conclusions are valid for elemental metals, but not necessarily true for compounds of these metals.

Emissions in Bed Solids. Table 13 shows the inorganic analysis of the bed reject solids. Several toxic metals exceed MATE values, although their compound form may be less toxic than implied by the comparison. The anion analysis indicates the degree of conversion from carbonate to sulfate within the bed. Table 14 shows the trace metal content of this material. Whether the chemical form in which the metals are present is an unacceptable hazard for simple land disposal still needs

TABLE 12. INORGANIC ANALYSIS OF PARTICULATE EMISSIONS

Substance	Size Range 1-3 μ	Size Range 3-10 μ	Land MATE	Is Land MATE Exceeded at Observed Value	Is Land MATE Exceeded at 1/100 Observed Value
	Volatile and Toxic Elements, μg/g[(a)]				
As	45	36	0.1	Yes	Yes
Be	15	11	0.03	Yes	Yes
Cd	2.1	1.3	0.004	Yes	Yes
Hg	<0.02	<0.02	0.02	No	No
Pb	44	43	0.1	Yes	Yes
Sb	4.0	2.3	0.4	Yes	No
Se	27	22	0.05	Yes	Yes
Te	<0.5	<0.5	3.0	No	No
	Major Elements, μg/g				
Al	200,000	200,000	2.0	Yes	Yes
Fe	60,000	20,000	0.5	Yes	Yes
Si	200,000	200,000	300	Yes	Yes
K	3,000	1,500	1720	Yes	No
Ca	30,000	30,000	32.4	Yes	Yes
C (total carbon)	12,000	11,000			
	Anions, weight percent				
Cl^-	0.011	0.007			
F^-	0.031	0.032			
$CO_3^=$	<0.2	<0.2			
$SO_4^=$	9.4	8.7			
$SO_3^=$	0.001	0.004			
$S^=$	<0.03	0.03			
NO_3^-	<0.001	<0.001			
NO_2^-	<0.001	<0.001			

(a) Atomic Absorption Spectroscopy Method used except for As which was determined colorimetrically.

to be determined. The concentration of polycyclic organic materials was found to be insignificant, as shown in Table 15. The organic constituents in the bed reject material pose no environmental problem for land disposal. Table 15 also shows the content of hydrocarbons with more than six carbon atoms; these amounts appear fairly low.

TABLE 13. INORGANIC CHEMICAL ANALYSIS OF BED REJECT MATERIAL

Substance	Observed Value	Land MATE	Observation Exceeds MATE
Volatile and Toxic Elements, μg/g[(a)]			
As	21	0.1	Yes
Be	2.7	0.03	Yes
Cd	.44	0.004	Yes
Hg	<0.02	0.02	No
Pb	8.0	0.1	Yes
Se	0.8	0.05	Yes
Sb	0.5	0.4	Yes
Te	<0.5	3.0	No
Major Elements, μg/g			
Al	15,000	2.0	Yes
Fe	10,000	0.5	Yes
Si	15,000	300	Yes
K	10,000	1720	Yes
Ca	200,000	32.4	Yes
C (noncarbonate)	1,600		
Anions, weight percent			
Cl^-	.030		
F^-	.003		
$CO_3^=$	15.1		
$SO_4^=$	27.7		
$SO_3^=$	.011		
S^-	.005		
NO_2^-	<.001		
NO_3^-	<.001		

(a) Atomic Absorption Spectroscopy Method used except for As which was determined colorimetrically.

Leachates From Bed Reject Materials. Leachates were generated in the laboratory using the spent bed materials (SBM). The 720-hour shake method was employed. This method involved shaking 33 grams of SBM with 100 ml of triple-distilled water for 72 hours in a reciprocating shaker at 120 cycles/minute. After 72 hours, the liquid was decanted and saved. A fresh 100 ml of distilled water was again added to the same SBM sample. This process was repeated 10 times to get 720 hours of shaking and 1000 ml of decanted leachates. By the same procedure, leachates were generated from the fly ash sample collected from the second cyclone. Both leachates were analyzed for inorganics, using Level 1 techniques (SSMS) for elements. Some Level 2 techniques (wet chemistry or atomic absorption spectroscopy) were employed to determine antimony, mercury and arsenic. Leachates were also analyzed for anions ($SO_4^=$, $SO_3^=$, etc.) by standard wet chemistry. Organics were analyzed by Level 1 techniques (liquid chromatography separation and infrared analysis). Significant results of inorganic analysis are presented in Table 16 in comparison with water MATEs (based on ecological effects). These results show that As, Ca, Ni, Pb, Li, Se, $SO_4^=$ and Al are present in concentrations equal to or exceeding the MATEs. Hence, these substances should be analyzed by Level 2 techniques in future leachate studies to accurately establish their concentrations and environmental effects. Also, the compound forms in which they are present should be investigated.

The results of organic analysis were not as conclusive and further work is needed to determine which specific organic compounds in leachates are present in harmful amounts.

Leachate Analysis and the RCRA. The importance of the above results to FBC waste disposal will be determined by comparing the leachate analyses with the requirements proposed under the Resource Conservation and Recovery Act (RCRA). Under Section 3001 of RCRA, waste will be defined as hazardous if it is inflammable, corrosive, infectious, reactive, radioactive, or toxic. Of these criteria, corrosivity, reactivity, and toxicity are likely to be pertinent to FBC residue.

Based on draft RCRA guidelines, FBC waste will be considered corrosive if a saturated solution of the residue in water has a pH of less than 2 or greater than 12. The results in Table 16 showed the leachate from spent bed material to have a pH of 12.2 (corrosive). The pH of a saturated solution could be expected to be somewhat higher. However, the pH of the fly ash leachate was only 9.0. Therefore, if disposed together, the mixture of fly ash and spent bed material may not be corrosive.

According to draft RCRA guidelines, FBC residue will be considered toxic if its leachate (to be generated by a "standard" method, not yet determined):

(a) has a concentration of any substance greater than or equal to 10 times the drinking water standard

(b) has a concentration of any substance greater than or equal to 0.35 times the lowest oral mammalian LD_{50} (mg/kg) for that substance, as listed in the NIOSH Registry of Toxic Effects of Chemical Substances

TABLE 14. TRACE METALS IN BED REJECT MATERIAL[a]

Element	MATE Value for Land 1 Minimum Value µg/g	Observation Exceeds MATE	Observation µg/g	Element	MATE Value for Land 1 Minimum Value µg/g	Observation Exceeds MATE	Observation µg/g
Li	0.51	Yes	200	Ag	0.500	Yes	≤0.1
Be	0.0300	Yes	0.3	Cd	0.00400	Yes	<0.5
B	324		30	In	3		<0.6
F	75		0.3	Sn	3		2
Na	90	Yes	300	Sb	0.400	Yes	1
Mg	36.5	Yes	20%	Te	3		<0.4
Al	2	Yes	1.5%	I	30		<0.07
Si	21	Yes	1.5%	Cs	2460		4
P	0.001	Yes	50	Ba	2.20	Yes	30
S	--		1.5%	La	--		7
Cl	0.0200	Yes	40	Ce	38.4		7
K	1720		1%	Pr	1540		1
Ca	32.4	Yes	20%	Nd	1580		1.5
Sc	1610		3	Sm	--		0.5
Ti	2	Yes	200	Eu	--		3
V	0.300	Yes	20	Gd	--		1
Cr	0.5	Yes	30	Tb	--		0.3
Mn	0.200	Yes	100	Dy	380		<0.1
Fe	0.500	Yes	1%	Ho	--		<0.3
Co	3	Yes	1.5	Er	--		<0.1
Ni	0.02	Yes	150	Tm	--		<0.3
Cu	1	Yes	15	Yb	--		≤0.3
Zn	1	Yes	400	Lu	--		≤0.3
Ga	14.9	Yes	7	Hf	1.50		≤0.3
Ge	18	Yes	40	Ta	150		<0.4
As	0.100	Yes	20	W	30		<0.4
Se	0.05	Yes	3	Re	--		<0.4
Br	1	Yes	3	Os	--		<0.2
Rb	3640		60	Ir	--		<0.4
Sr	92.2		300	Pt	0.0600	Yes	<0.1
Y	30		1.5	Au	--		<0.4
Zr	15		0.5	Hg	0.0200	Yes	<0.2
Nb	650		2	Tl	0.5	Yes	2
Mo	14		<1	Pb	0.100	Yes	<0.15
Ru			<1	Bi	23800		0.2
Rh	0.300	Yes	<0.5	Tn	1.26		0.4
Pd	--	Yes		U	6		

(a) Spark source mass spectrographic analysis.

TABLE 15. ORGANIC CHEMICAL ANALYSIS OF BED REJECT MATERIALS

Substances	Land MATE	Observation
Polycyclic Organic Materials, ng/g		
Anthracene/phenanthrene	14,500	<0.1
Others specifically sought	No data	<0.1
Total		--
Hydrocarbon Content Above C6, µg/g		
Hydrocarbon according to boiling point range		
C7	No data	20
C8	Ditto	22
C9	"	12
C10	"	4
C11	"	5
C12	"	3
>C12	"	17
Reduced Sulfur and Other Compounds		
Reduced sulfur, µg/g	No data	<0.2
Other compounds detected	Ditto	None

TABLE 16. INORGANICS IN LEACHATES FROM SPENT BED MATERIAL (SBM) AND FLY ASH (FA)

Substance or Parameter	Concentration, mg/l		Water MATE mg/l	MATE Exceeded?
	SBM	FA		
Li	6	20	0.38	Yes
Na	10.4	52	800	No
Mg	9.6	6.4	87	No
Al	0.8	1.4	1.0	Yes
Ca	460	1000	16.2	Yes
V	0.1	0.1	0.15	No
Fe	0.2	0.2	0.25	No
Ni	0.03	0.03	0.01	Yes
Se	0.07	0.07	0.025	Yes
Pb	0.05	0.05	0.05	No
As	0.04	0.05	0.05	No
CN^-	<0.03	<0.03	0.015	Undecided
$SO_4^=$	1610	1950	250(a)	Yes
pH	12.2	9.0	5-9(a)	Yes

(a) Proposed US EPA drinking water standards; no MATE value available.

TABLE 17. RESULTS OF THE BIOLOGICAL TESTING OF FBC WASTE STREAMS

Test	Test Parameter	Waste Streams			
		Flue Gas	Suspended Particulates	Bed Solids	Bed Solids Leachate
Ames	+/-		+	-	-
Cytotoxicity					
WI-38	LD_{50}				
RAM	LD_{50}		NA	NA	NA
Rodent Acute Toxicity	LD_{50}			NT	NT
Aquatic					
Freshwater					
Algal	EC_{50}				45%
Daphnia	LC_{50}				40.9%
Fish	LC_{50}				25.3%
Saltwater					
Algal	EC_{50}				NT
Shrimp	LC_{50}				NT
Fish	LC_{50}				NT
Terrestrial Soil Microcosm	Ranked in order of toxicity		2	3	1
Stress Ethylene	Percent of increase over control	0%			

NA = Not available.
NT = No toxicity.

(c) has a concentration of any substance equal to 10 times the lowest 96-hour LC_{50} (mg/l) for that substance, as listed in the NIOSH Registry.

In these studies, none of the primary drinking water standards are exceeded by a factor of 10 by either leachate. However, the results still must be measured against criteria (b) and (c) above.

If the MATE values for calcium are similar to the primary drirking water standards, calcium in leachates may well exceed the allowable standards by more than a factor of 10, thereby causing the FBC residues to be considered hazardous.

The importance of the designation "hazardous" lies in the somewhat stricter disposal requirements likely to be imposed, and the additional permits, testing, and record-keeping required by RCRA.

Bioassay Results. The biological test results for four FBC waste streams are given in Table 17. The health and ecological tests on each stream were performed according to the pilot Level 1 bioassay program. The results of the cytotoxicity tests are still being processed at this time.

The flue gas stream was tested only with the stress ethylene test. At present, no other Level 1 tests are suitable for testing gases. Results indicate the gas was nontoxic. Some caution is associated with this conclusion because the full quantity of gas required for the test was not available and the sample had to be stored for some time before testing.

Several tests were performed on the spent bed solids. This stream showed very low or no toxicity in all tests, and would not likely constitute a biological hazard in its solid form. The leachate from the spent bed solids showed some toxicity in two of the tests. The results show that it was nontoxic to mammals (health tests) and marine organisms, but toxic to freshwater and soil organisms. This stream would likely require further study to determine its potential biological hazard.

Only the suspended particulates stream gave positive Ames test results. The particulates were mutagenic and thus may also be carcinogenic. This stream was also toxic to soil organisms.

Based on the biological tests alone, the relative ranking of the four waste streams, in order of decreasing toxicity, is:

(a) Spent bed solids leachate

(2) Suspended particulates

(3) Spent bed solids

(4) Flue gas.

It must be emphasized that the test results provide only relative data, and the actual hazard to humans and other organisms can be determined only through additional testing.

Summary and Conclusions on Comprehensive Analysis Results

On Source Emission Data

The major conclusion is that comprehensive analysis of emissions from emerging energy technologies yields useful results for completing the environmental assessment of the processes. Other conclusions are:

(1) Pressurized coal-burning FBC units can meet existing New Source Performance Standards for SO_2 and NO_x emissions from coal-fired steam generators. Particulate emissions control needs demonstration.

(2) MATEs for SO_2, NO_x, CO and possibly for other substances need reevaluation.

(3) Polycyclic organic matter (POMs) in flue gas or other effluents from FBC units do not appear to be health/ecological hazards. POMs are concentrated in fine particles (<3 microns) as opposed to coarse (>3 micron) particles in the suspended particulates.

(4) Though biological assay data are difficult to interpret at this stage, spent bed material leachate and suspended particulates do show a relative higher toxicity than flue gas and bed solids. This trend corresponds with the greater than MATEs concentrations of many volatile and toxic trace elements (As, Ni, Pb, Li, etc.) in leachates from bed materials. These results, therefore, indicate the need for further study. The final interpretation of the bioassay results and their toxicity ratings is being considered by the US EPA.

(5) The results of this study do not imply that fluidized-bed combustion of coal generates solid wastes of greater or lesser toxicity than other methods of coal combustion, since the solid wastes from other methods have not been subjected to such comprehensive analysis. Also, the above results need careful evaluation and further validation.

Careful attention to insure steady-state operation of the process is necessary before beginning sampling. Adequate steps to insure sufficient coal/sorbent supply of uniform composition to last the duration of sampling is important for obtaining useful and reliable data.

Acknowledgments

The studies described in this paper are part of the environmental assessment of the fluidized-bed combustion process which Battelle is conducting for the US EPA, under the guidance of R. P. Hangebrauck and D. Bruce Henschel of the Agency's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina. The comprehensive analyses of emissions were conducted in cooperation with many individuals of EXXON. The authors sincerely appreciate the assistance and support of all these persons.

List of Acronyms

CA	Comprehensive Analysis
FBC	Fluidized-Bed Combustion
SASS	Source Assessment Sampling System
SSMS	Spark Source Mass Spectroscopy
AAS	Atomic Absorption Spectrometry
AAS/GF	Atomic Absorption Spectrometry/ Graphite Furnace Atomization
AAS/HG	Atomic Absorption Spectrometry/ Hydride Generation
ASTM	American Society for Testing and Materials
FAAS	Flameless Atomic Absorption Spectrometry
POM	Polycyclic Organic Matter
LRMS	Low Resolution Mass Spectrometry
GC/MS	Gas Chromatography
GC/FPD	Gas Chromatography/Flame Photometric Detection
GC/FID	Gas Chromatography/Flame Ionization Detection
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
NBS	National Bureau of Standards
SRM	Standard Reference Materials
LLL	Lawrence Livermore Laboratory
ORNL	Oak Ridge National Laboratory
MATE	Minimal Acute Toxicity Effluent
RCRA	Resource Conservation and Recovery Act
NIOSH	National Institute for Occupational Safety and Health

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ENVIRONMENTAL ASSESSMENT PROGRAM FOR THE HYGAS PROCESS

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ABSTRACT

The main objective of the HYGAS® Environmental Assessment Program is to systematically obtain and interpret experimental data from the HYGAS pilot plant to estimate pollutant production for demonstration and commercial-scale HYGAS coal gasification plants. Priorities have been established for operating systems for sampling, analyses, and data evaluation to define the fate of potential pollutants generated during pilot plant operation. The assessment methodology for environmental data acquisition and interpretation features these sequential objectives:

- identification of potential pollutants in plant effluent streams,
- development of sampling, preservation, and analytical techniques,
- process unit, stream, and species selection, and
- quantitative descriptions of significant pollutants.

Introduction

The Institute of Gas Technology (IGT) is performing an environmental assessment of the HYGAS Process under contract to the U. S. Department of Energy (DOE). HYGAS is a second-generation coal gasification process which uses hydrogen in a fluidized bed at high pressures and temperatures to maximize production of high-Btu substitute natural gas (mostly methane) from all types of coal. About two-thirds of the total methane produced in the process is generated by direct conversion in the gasifier.

The process is currently being developed at the HYGAS pilot plant under funding from DOE and the American Gas Association. The pilot plant has a design capacity of 3 tons/hr of coal to produce a nominal 1.5×10^6 SCF/day of pipeline quality gas at 1000 Btu/SCF. The main objective of the HYGAS Environmental Assessment Program is to systematically obtain and interpret experimental data from the pilot plant to estimate pollutant production from demonstration- and commercial-scale HYGAS coal gasification plants. Priorities have been established for operating systems for sampling, analysis, and data evaluation to define the fate of potential pollutants generated during pilot plant operation.

The HYGAS Process

Figure 1 shows the current processing steps and the major plant streams for the HYGAS pilot plant. After the coal is crushed and dried, the pretreatment step is used only for agglomerating coals, as pretreatment is a mild surface oxidation used to destroy agglomerating tendencies. Coal is introduced into the high-pressure reactor in a light oil slurry containing up to 45 weight percent coal. The coal passes through four fluidized beds during gasification and spent char is removed from the bottom of the gasifier. Crude product gas leaves the gasifier and passes through a cyclone separator to a quench system for the separation, recovery, and recycling of both the light oil and water. Acid gases (H_2S and CO_2) are removed from the cooled product gas with a diglycolamine-water solution which is regenerated and recycled. Subsequent washing steps further prepare the gas for upgrading to essentially pure methane (SNG) by methanation of residual CO and H_2 in a packed bed of nickel catalyst.

The Environmental Assessment Program

Pilot Plant Sections of Interest

The environmental assessment is being focused upon portions of the pilot plant considered "scaleable" to larger plant designs (Figure 1). A scaleable unit is defined as an existing pilot plant unit which will have a duplicate counterpart in a demonstration or commercial HYGAS plant (such as the pretreater and the hydrogasifier). Other parts of the pilot plant (such as the wastewater treatment section) are designed specifically for pilot plant operation and are not scaleable.

Because a wide variety of process designs and flow sheets can be expected for the demonstration and commercial plants, many HYGAS process variations are being considered and evaluated. A methodical chemical engineering analysis of existing facilities is necessary to characterize probable pollutant distributions in streams designed into the large-scale plants.

Definition of Steady-State Operation

Data acquisition from the pilot plant requires defining the concept of "steady-state operation". Normal operation of developmental pilot plants, such as HYGAS, is intermittent with considerable periods of unsteady operation. Problems hampering continuous operation include process upsets and mechanical failures. The criteria for "steady-state" operation has been defined by HYGAS plant operators according to the following sequence:

- steady feed rates (of coal or pretreated char) to the gasifier,
- constant density of feed slurry to the gasifier,

- self-sustained operation of the gasifier (that is, all heating requirements for the gasification reactions are supplied by the steam-oxygen section with no external heating),
- steady fluidized-bed levels in the four beds of the reactor,
- essentially constant off-gas composition and solids flow rate from the gasifier, and
- steady operation of downstream process units, such as the quench and light oil stripping sections, which influence operation of the gasifier.

All pilot plant recording instruments transmit process data to a central data processing system which files the inputs for future retrieval and data reduction by computer calculations. Steady-state periods are defined during a subsequent review of the operating data and are normally identified after completion of each HYGAS test.

Sampling Techniques

Once steady-state, self-sustained operation is achieved in a specific HYGAS test, routine grab sampling of the process water, solids, and oil streams is started. In addition to specialized sampling for specific purposes (such as time series studies for specific pollutants), on-line analytical instrumentation is also being developed to study sulfur species in process gas streams plus total organic carbon (TOC) and total oxygen demand (TOD) in process water streams. Techniques which are currently applicable to the analyses of solid, liquid, and gaseous phases are listed in Table 1.

Sample Preservation

Analyzing HYGAS wastewater samples presents significant problems because known preservation and analytical techniques are not effective for all species. HYGAS wastewaters are not unique in this respect; similar results have been observed in other coal gasification plants. State-of-the-art procedures developed in earlier HYGAS work were the starting point for analyzing the water samples. Appropriate refinements to the wet-chemical water analyses have been made due to continuing laboratory studies of preservation and analytical techniques at IGT and Carnegie Mellon University (CMU). Efforts to improve sample preservation and analysis at each of the coal gasification pilot plants are being coordinated by CMU.

The cooperative efforts between IGT and CMU have established that current preservation methods for the water samples prevent significant degradation with storage time and that HYGAS samples can be analyzed off-site, preferably within 24 to 72 hours after collection. The comprehensive data base includes sets of daily mean concentration values for each pollutant in each water stream as well as simultaneous process conditions such as pressures, temperatures, and flow rates. These data are later evaluated to normalize the results to obtain pollutant production rates in terms of coal feed on a moisture and ash free basis. A set of interim results for a recent HYGAS test with Illinois bituminous coal is given in Table 2. These data are not yet final because the process data are still being refined and applied to the normalization procedure.

Sulfur-by-Species Analyses

A sulfur-by-species analysis has been conducted on the process solids streams as part of the environmental assessment. These solids have included the coal feed, the pretreated char, the spent char, and char from the first and second gasification stages.

The gasification of sulfur by species for one HYGAS test, from fresh coal feed to the pretreater through the gasified spent char, is reported in Table 3. Overall, the sulfur gasified in this HYGAS test was 27% during pretreatment, 69% and 79% for the first and second gasification stages, respectively, and 96% for the spent char. Pretreatment was more severe than expected under optimized conditions because gasifier operability was the main objective for this HYGAS test.

Minor and Trace Elements

The fate of minor and trace elements in the solids is also being monitored during the pretreatment and gasification steps. These trace element recoveries in solids obtained from gasification of subbituminous coal (with no pretreatment) are shown in Table 4. As shown in the table, these elements can be grouped into several categories according to their recovery in the spent char. In these tests, the more volatile elements were chlorine, mercury, selenium, and (in one test) cadmium. The trace elements are expected to exhibit individual reactivities in the various gasification steps, depending on the chemical state of the elemental species and the processing conditions (such as large temperature differences and oxidizing or reducing atmospheres). The HYGAS process is not unique in this respect, but is comparable to other industrial processes (power plants, steel mills, glass plants and other coal gasification processes) where large temperature gradients exist.

Light-Oil Composition

The light oil used to slurry the coal feed for introduction into the high-pressure gasifier is being sampled and analyzed by GCMS techniques for organic composition. This oil is recovered and recycled during each pilot plant test. The HYGAS process will produce a net make of light oil (benzene, toluene, and xylene) and toluene is used in the pilot plant to represent the oil product. The oil used in the coal feed slurry represents a concentrated source of polynuclear aromatics, potential carcinogens, and potentially toxic organic compounds. As each HYGAS test progresses, this oil changes in composition as a function of operating time and processing conditions.

Changes in composition as a function of operating time and coal type are shown by the data in Table 5. The differences in oil composition near the beginning of a test occur because the plant inventory of approximately 6000 gallons remaining after a pilot plant test is reused to slurry the coal feed for the subsequent test.

Conclusion

A brief overview of the environmental assessment program for the HYGAS process has been presented. Data from this program are now providing a strong baseline characterization of pollutant species in major process streams. The program is now entering an advanced phase which requires a more thorough material balance characterization of specific pollutants around the scaleable HYGAS pilot plant units.

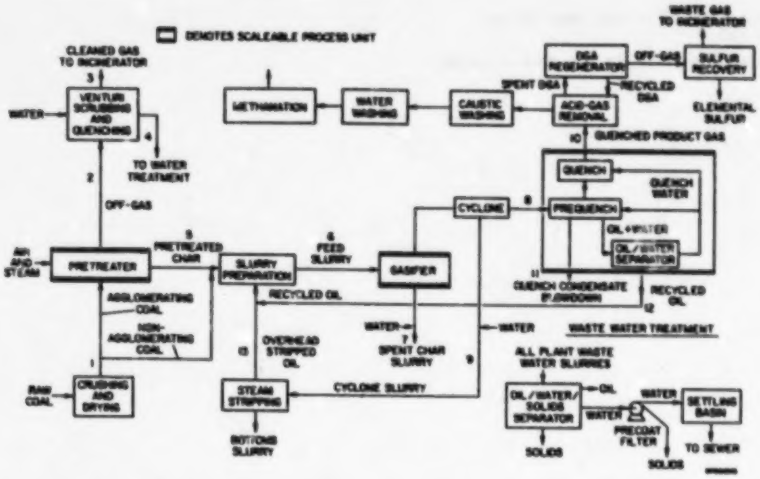
DENOTES SCALEABLE PROCESS UNIT
CLEANED GAS TO INCINERATOR
3
WATER
VENTURI SCRUBBING AND QUENCHING
4
TO WATER TREATMENT
2
OFF-GAS
METHANATION
WATER WASHING
CAUSTIC WASHING
ACID-GAS REMOVAL
SPENT DGA
RECYCLED DGA
DGA REGENERATOR
OFF-GAS
SULFUR RECOVERY
WASTE GAS TO INCINERATOR
ELEMENTAL SULFUR
10
QUENCHED PRODUCT GAS
QUENCH
QUENCH WATER
PREQUENCH
OIL+WATER
OIL/WATER SEPARATOR
CYCLONE
8
AIR AND STEAM
PRETREATER
5
PRETREATED CHAR
SLURRY PREPARATION
6
FEED SLURRY
GASIFIER
11
QUENCH CONDENSATE BLOWDOWN
RECYCLED OIL
12
RECYCLED OIL
AGGLOMERATING COAL
NON-AGGLOMERATING COAL
1
RAW COAL
CRUSHING AND DRYING
13
OVERHEAD STRIPPED OIL
STEAM STRIPPING
BOTTOMS SLURRY
WATER
7
SPENT CHAR SLURRY
9
WATER
CYCLONE SLURRY
WASTE WATER TREATMENT
ALL PLANT WASTE WATER SLURRIES
OIL/WATER/SOLIDS SEPARATOR
OIL
WATER
WATER
PRECOAT FILTER
SETTLING BASIN
SOLIDS
SOLIDS
TO SEWER

Figure 1. SCALEABLE PROCESS UNITS AND MAJOR STREAMS IN THE HYGAS PILOT PLANT (Major Streams: Reference Numbers 1-13)

Table 1. SUMMARY OF APPLIED ANALYTICAL TECHNIQUES FOR HYGAS PROCESS STREAM CHARACTERIZATION

	Species Identified	
Technique	Environmentally Related	Other
	Gas Phase	
Mass Spectroscopy[1]		
Gas Chromatography	Sulfur Species	Hydrocarbons
Sulfur Chromatograph[2]	H_2S, COS, CS_2, CH_3SH, CH_3SSCH_3, CH_3SCH_3, $CH_3SCH_2CH_3$, SO_2, t-Butyl Mercaptans	
Atomic Absorption	Trace Elements Metal Carbonyls	
Hydrocarbon Chromatograph	H_2S, CO	H_2, CO_2, C_2H_6, Ar, N_2, CH_4
	Liquid Phase	
Mass Spectroscopy		
Atomic Absorption	Trace Elements	
GCMS[3]	Trace Organics (PNA)	Non-Methane Hydrocarbons
TOC Analyzer[2]	TOC	
TOD Analyzer[2]	TOD, (COD, BOD)	
Wet-Lab Analysis	CN^-, NH_3, NO_3^-, F^-, $PO_4^{\equiv}$, $S^=$, COD, BOD_5, Phenols, TOC, Grease & Oil	TDS, Hardness Alkalinity, Dissolved Oxygen, TSS, pH, Cl^-, TOD, S-Total, N-total, SCN^-, $SO_3^=$, $SO_4^=$
	Solid Phase	
Mass Spectroscopy		
Atomic Absorption	Minor and Trace Elements	
X-Ray Diffraction	Minor and Trace Leachates	
Wet-Lab Analysis	S – total N – total	
Sieve Analysis	Particulates	
Ultimate & Proximate Analysis	S-Total N-Total	% Ash, % Volatiles % Moisture Heat Value

1. Empirical analysis of all listed species.
2. On-line continuous analyzer.
3. Gas Chromatograph-Mass Spectrometer.

Table 2. WATER-SOLUABLE POLLUTANT PRODUCTION: HYGAS TEST 64, ILLINOIS NO 6 COAL FROM PEABODY MINE 10 (INTERIM RESULTS)

Species	Pretreater lb/Ton Coal (MAF)	Gasifier lb/Ton Char (MAF)
Total Dissolved Solids	67	11
Phenols	5.2	10.2
Cyanide	0.0002	0.0006
Total Organic Carbon	12	20
Thiocyanate	1.7	1.1
Sulfide	0.0004	3.3
Ammonia-Nitrogen	0.4	24.9
Chloride	3.4	1.2

Table 3. GASIFICATION OF SULFUR BY SPECIES FOR HYGAS TEST 64, WITH ILLINOIS BITUMINOUS COAL

	Coal Feed	Spent Char	Sulfur Gasified
	—lb Sulfur/100 lb Coal Feed—		%
Sulfide	0.04	0.012	71
Sulfate	0.21	0.007	97
Organic	2.57	0.159	94
Pyritic	1.71	0.022	99
Total	4.53	0.200	96

Table 4. TRACE ELEMENT[a] RECOVERY IN SPENT CHAR

HYGAS TESTS 55 AND 58: ROSEBUD SUBBITUMINOUS COAL

90 TO 100%
Be, V, Mn, Zn, Li, Cr, Pb,[b] Ba, Cd, Ni

50 TO 90%
As, B, Cu, F, Fe, Mo, Tl, Ba, Ni, Pb

LESS THAN 50%
Cl, Hg, Se, Cd

[a] Elements below detection limits in both feed and char were Sb, Co, Te, and Sn.

[b] Underlined elements could be placed in more than one group.

Table 5. LIGHT OIL COMPOSITION IN HYGAS COAL-FEED SLURRY

Coal Type	Lignite		Subbituminous	
Days of Operation	1	12	2	12
	wt%			
Aliphatics	0.5	1.1	6.8	7.3
Aromatics				
One-Ring	97.5	96.6	85.7	84.6
Two-Ring	0.7	1.8	5.0	5.5
Three-Ring	0.06	0.1	0.9	0.8
Four-Ring	0.013	0.027	0.21	0.13
Five-Ring	—	—	0.01	0.004
Miscellaneous	—	—	0.7	0.7
Unknowns	1.2	0.3	0.6	0.8

ANALYSIS OF SYNTHANE/SYNTHOIL PRODUCTS

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Abstract

An overview of the compositional data for the main streams from coal gasification and coal liquefaction processes, important for environmental as well as process development considerations, is given. A summary of the information available concerning the chemical constitution of coal, derived by some of the latest spectral techniques, is presented. Challenges for the analyst in terms of developing methods to obtain data required for product characterization for some of the newer fossil energy processes are highlighted.

Introduction

Increased emphasis on developing processes for substitute gaseous and liquid fuels from coal has highlighted the need for additional compositional data for coal as well as for many of the process streams. The purpose of this contribution is to summarize some of the latest information concerning the so-called chemical structure of coal as determined by newer spectral techniques and to give an overview of the composition of the streams common to many gasification and liquefaction processes under development.

Data from the SYNTHANE PDU gasifier(1) and 1/2 ton per day liquefaction unit(2) at the Pittsburgh Energy Research Center are used to describe the composition of the various process streams. Table 1 shows the process streams from the SYNTHANE gasifier including, in addition to the feed coal, the gas, char, condensate water, and tar. Streams from the liquefaction PDU are shown in Table 2 and include the feed coal, the feed paste, which is a mixture of feed coal and recycle oil from the centrifuged liquid product, the raw product, centrifuged residue consisting of unreacted coal and mineral matter and some of the scrubber effluents.

Discussion

Structure of Coal

The structure of coal was a major topic for research both here and abroad in the 1950's and early 1960's. During the 1960's and extending into the 1970's, the study of basic coal chemistry decreased; the remaining effort was concentrated in a few laboratories, including the U. S. Bureau of Mines at Bruceton, Pennsylvania.

The following is a summary of information obtained from a number of sources including the Chemistry of Coal Utilization and the Supplementary Volume by Lowry,(3) books by Francis(4) and van Krevelen,(5) several publications by Given(6) and others, and a recent excellent review by J. Gibson delivered as the Robens Coal Science Lecture in 1977.(7) Also included are results of several studies at the Pittsburgh Energy Research Center.

Reflectance and x-ray diffraction are two of the techniques used extensively in early studies of the structure of coal. Reflectance has the advantage that individual particles can be investigated as against bulk property determinations by most other techniques. Reflectance is related to the refractive index which in turn is related to the molar refractivity, an additive property of atoms and bonds. Coking ability and similar utilization information can be inferred from reflectance measurements.

X-ray data show that coal is not crystalline but contains much amorphous material depending on the rank of the coal. The types of information that can be provided by x-ray diffraction are the sizes of the layers and the number of layers in parallel stacks. The consensus of information derived by Hirsch and coworkers(8) indicates that in the 78 to 94 percent carbon range the largest clusters of atoms contain approximately 32 atoms. The amorphous content decreases with increasing rank. Low rank coals have small layers that are randomly oriented. Medium rank coals show layers of moderate orientation, while high rank coals into the anthracite range contain the largest layers and have a high degree of orientation.

Aromaticity (f_a = aromatic carbon/total carbon) can be derived by a number of techniques including magnetic resonance, density determinations, sound velocity, heats of combustion and ultraviolet spectrophotometry. The range in f_a is from approximately .7 for low rank coal to 1 for the higher rank coals. These data were derived primarily from x-ray determinations by Hirsch and coworkers.(8) J. K. Brown(9) obtained hydrogen aromaticity values from infrared spectra. In low rank coals about 80 percent of the hydrogens are on aliphatic carbons while anthracitic coals show essentially zero association of hydrogens with aliphatic carbons.

Data for the heteroatoms, oxygen, nitrogen and sulfur, are meager and less authentic than for carbon and hydrogen. Total oxygen is determined by difference. Unweathered coals do not indicate carbonyl oxygen. At present there is no direct way to establish how nitrogen and sulfur occur in coals. The information obtained thus far has been derived from pyrolysis products such as tars or from extracts of coals. Pyridine nucleus compounds predominate and benzothiophene is many times used as a model for the sulfur in coal. Coal liquefaction products contain both basic and acidic nitrogen in the form of pyridine nucleus compounds and carbazoles.(10)

Information concerning possible hydroaromatic rings in coals has been obtained by catalytic dehydrogenation and other methods. The indications are that 40 to 50 percent of the total hydrogen in bituminous coal is in hydroaromatic rings.(11)

Vapor phase osmometry and other techniques have been used to determine the molecular weight of solubilized material from coals. Intermolecular interactions can lead to erroneous results but values have ranged up to several thousand.

Several attempts have been made to reconcile the somewhat divergent data concerning the aromaticity of coal. As previously mentioned, Hirsch and coworkers have evidence from x-ray data that the carbon atoms in coal are primarily aromatic while the infrared data of Brown concerning the distribution of hydrogen atoms indicates that the hydrogen is primarily associated with aliphatic carbons. Given,(6) Gibson(7) and Hill(12) have proposed models that incorporate much of the structural information derived by a variety of techniques. Perhaps the most popular model is that proposed by Given in 1960 in which he used an 82% carbon coal and the associated data to derive his model. The carbon aromaticity of the model was .69, consistent with much of the data for coal with this carbon content. The mean structural unit used in Given's model contains two condensed rings.

Composition of Coal Gasification Products

Mass spectrometry has played a major role in the analysis of coal gasification product streams. Gas analysis methods, including techniques for the analysis of trace and minor components, were standardized by the petroleum laboratories in the 1940's. Analyses of several streams from the SYNTHANE process are used to illustrate the application of mass spectrometry to coal gasification products. In addition to the major gaseous components (i.e., hydrogen, methane, carbon monoxide, ethane, and carbon dioxide), Table 3 lists the concentrations of trace components found in a typical product gas.(13) Hydrogen sulfide, at 6500 ppm, is of the greatest concern from the environmental point of view. An analysis of the methylene chloride extract of a condensate water is shown in Table 4.(14) The extract is in the range of 0.6 to 2.4 weight percent of the water; 60 to 80 percent of the extract is phenolic in character. A relatively small amount of tar, highly aromatic in nature, is also formed as a by-product of coal gasification; a low ionizing voltage analysis of this tar is shown in Table 5.(13) An appreciable quantity of heterocyclic material containing oxygen, nitrogen, and sulfur has been identified.

Composition of Coal Liquefaction Products

The analysis of coal liquefaction products requires a combination of solvent fractionation, chromatographic separation, and chemical derivatization prior to application of spectrometric methods, including infrared and mass spectrometry. The centrifuged liquid product (CLP) from the 1/2 TPD liquefaction unit at the Pittsburgh Energy Research Center is used to illustrate the analytical techniques involved. The first solvent separation, with benzene and pentane (hexane and cyclohexane have also been used) yields a heavy oil and an asphaltene fraction. The heavy oil, ~70% of the CLP, is further separated, using the SARA technique(15) or other chromatographic methods, into saturate, aromatic, basic nitrogen, neutral nitrogen, and acid (phenolic) fractions. The saturate and aromatic fractions are amenable to mass spectrometric type-analysis methods developed for petroleum and coal liquefaction products.(16)(17) Table 6 shows a typical analysis of a heavy oil, combining the mass spectral data for the saturate and aromatic fractions with the chromatographic data for the other fractions. The nitrogen heterocyclics have been analyzed by low ionizing voltage;(10) the oxygen-containing species have been classified as alkylated phenols, indanols/tetralinols, phenylphenols, and cyclohexylphenols.(18) New analytical methods will be required to further identify the specific compounds present in these fractions. Methods are not available to determine the degree of hydrogenation of the various ring systems, particularly in the basic nitrogen fraction. Thin-layer chromatography and capillary gas chromatography are possibly the best solutions to this problem but are hindered by the lack of representative pure compounds with hydrogenated ring systems.

Screening for Hazardous Compounds

High-resolution mass spectral data (HRMS) are routinely computer processed to obtain the precise masses and elemental compositions of all ions in a mass spectrum. To screen for toxic or hazardous compounds, an array of the precise masses of approximately 300 chemicals whose toxic limit values are known was added to the mass spectral data processing program. Screening is effected by computer matching the experimental masses against the toxic compound masses contained in the reference list. While the elemental composition can be determined, the particular isomeric form cannot be identified by HRMS data alone. This preliminary screening, however, limits the number and class of possible hazardous compounds that must be considered, thus defining the analytical determinations required for specific identification. Table 7 lists a portion of the screening data obtained for coal liquefaction process streams.(19)

Summary

Analytical problems concerned with the conversion of coal to gaseous and liquid fuels present many challenges to the analyst. These challenges are summarized in Table 8. Methods are needed for the direct determination of the physical and chemical properties of coal. Data for several of the prime species, such as the heteroatoms sulfur, oxygen and nitrogen, are obtained by indirect methods. Speciation is important particularly from the viewpoint of possible pollutants from the use of fossil fuels. The characterization of asphaltenes in coal-derived liquids is important as asphaltenes are thought by many to be intermediates in the conversion of coal to liquids. The extent of conversion is generally based on the yields of oil and asphaltenes. Currently, many methods are in use but standard methods are not available that could provide reliable comparisons of conversions from various processes. Only limited data for a few elements are available showing the fate of potentially hazardous elements in coal gasification and liquefaction processes. Elemental balances require determinations in various matrices and new methods must be developed. The concentration and nature of various heteroatoms, the source of many environmental pollutants, must be determined. Characterization of the heavy-ends is difficult, as many high molecular weight components with low volatility are included in the residues. Compositional data for the residues are important from the viewpoint of waste disposal. Many of the current coal conversion processes are catalytic and, particularly in the case of liquefaction, commercially available catalysts used in the petroleum industry are not adequate as deactivation occurs quickly. In summary, many of the standard methods available from the petroleum industry cannot be applied directly to coal-derived fuels and new methods must be developed.

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Table 1. Process Streams From a SYNTHANE Gasifier

Feed Coal
Gas
Char
Condensate Water
Tar

Table 2. Process Streams From a SYNTHOIL PDU

Feed Coal
Feed Paste
Recycle Oil (CLP)
Raw Product
Centrifuged Residue
Scrubber

Table 3. Trace Components in Gas From Coal Gasification

Compound	Concentration (ppm)
H_2S	6,500
COS	107
Benzene	480
Toluene	66
C_8 Aromatic	34
Thiophene	43
C_1-thiophene	24
C_2-thiophene	5
Methylmercaptan	80

Table 4. Condensate From Gasification of Illinois No. 6 Coal

Compound	Weight, ppm
Phenol	3400
Cresols	2840
C_2-phenols	1090
C_3-phenols	110
Dihydric phenols	250
Indanols Acetophenones	150
Hydroxybenzaldehyde Benzoic acids	60
Naphthols	160
Indenols	90
Biphenols	40
Benzothiophenols	110

Table 5. Mass Spectrometric Analyses of the Benzene Soluble Tar, SYNTHANE Gasifier

Structural type (including alkyl derivatives)[a]	Illinois No. 6 coal,[b] vol. %
Benzenes	2.1
Indenes	8.6[c]
Indans	1.9
Naphthalenes	11.6
Fluorenes	9.6
Acenaphthenes	13.5
3-ring aromatics	13.8
Phenylnaphthalenes	9.8
4-ring peri-condensed	7.2
4-ring cata-condensed	4.0
Phenols	2.8
Naphthols	[c]
Indanols	0.9
Acenaphthenols	-
Phenanthrols	2.7
Dibenzofurans	6.3
Dibenzothiophenes	3.5
Benzonaphthothiophenes	1.7
N-heterocyclics[d]	(10.8)

[a] Average molecular weight, 212.

[b] Spectra indicate traces of 5-ring aromatics.

[c] Includes any naphthol present (not resolved in these spectra).

[d] Data on N-free basis since isotope corrections were estimated.

Table 6. Typical Analysis of Hexane Soluble Material From a Coal Liquefaction Product

Compound Class	Type Analysis[a]	Compound Class	Type Analysis
Paraffins	1.7	Hexahydrophenanthrene	0.3
Non-condensed Naphthenes	1.0	Octahydrophenanthrene	2.3
2-ring Naphthenes	1.6	Dihydropyrene	3.6
3-ring Naphthenes	1.3	Pyrene/Fluoranthene	4.1
4-ring Naphthenes	1.1	Tetrahydrofluoranthene	2.7
5-ring Naphthenes	0.5	Hexahydropyrene	9.2
6-ring Naphthenes	0.2	Decahydropyrene	3.4
Benzenes	0.6	Chrysenes	1.5
Tetralins	7.1	5-ring peri-condensed	0.8
Naphthalenes	1.6	5-ring cata-condensed	0.5
Tetrahydroacenaphthenes	2.0	6-ring peri-condensed	0.5
Tetrahydrophenanthrene	11.9	Coronenes	0.6
Nitrogen Bases	14.6[b]	Neutral Nitrogens	8.3[b]
Acids-Phenolics	10.6[b]	Losses	6.4[b]

[a] Type analysis data derived from saturate and aromatic fractions. Methods are ASTM D-2786, C_{20} matrix and a tentative ASTM method for aromatic hydrocarbons.

[b] Data from SARA separation procedure.

Table 7. Screening of Coal Liquefaction Process Streams for Possible Hazardous Compounds

Precise Mass	Formula	Possible Hazardous or Toxic Compound(s)[a]	Feed Paste	Recycle Oil	Total Liquid Product	Centrifuged Liquid Product	Homogenized Residue	Org. Frac. Scrubber Effluent	Aqueous Ext. Scrubber Effluent
202.0780	$C_{16}H_{10}$	Pyrene	X	X	X	X	X		
213.1153	$C_{14}H_{15}NO$	4-Amino-4'-Hydroxy-azobenzene	X						
217.0891	$C_{16}H_{11}N$	1,2-Benzcarbazole	X	X		X	X		
228.0936	$C_{18}H_{12}$	Benz(a)anthracene Chrysene	X	X	X	X	X		
242.1095	$C_{19}H_{14}$	7-Methyl Benz(a)anthracene	X	X	X		X		
243.1048	$C_{18}H_{13}N$	Amino-1,2-Benzanthracene[b] (2)		X	X	X	X		
251.1674	$C_{18}H_{21}N$	Diethylamino Stilbene	X		X				
252.0936	$C_{20}H_{12}$	8,9-Ace-1,2 Benzanthracene 4,10-Ace-1,2 Benzanthracene 4,10-Benzo(a)pyrene	X	X	X	X	X		
254.1095	$C_{20}H_{14}$	Cholanthrene Acenaphthanthracene	X	X	X	X	X		
256.1252	$C_{20}H_{16}$	Meso-Dihydrocholanthrene Dimethyl Benz(a)anthracene (8)	X	X	X		X		

[a] Particular isomer not identified (see text).

[b] Number of alkyl isomers considered hazardous.

Table 8. Challenges for the Analyst

- Physical and chemical properties of coal
- Asphaltene determinations in coal liquids
- Fate of trace elements during coal conversion
- Quantitation of heteroatom species in coal liquids
- Characterization of heavy ends
- Identification of catalyst deactivating species

CHARACTERIZATION OF OIL SHALE PROCESSES

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Abstract

Experimental Characterization of an oil shale process is reported, based on an environmental sampling and analysis program conducted at the Paraho retorting operations. Multi-media sampling approaches are described. Analysis techniques are summarized with particular reference to shale oil process stream characteristics. Implications for future work are outlined.

Current Status

The development of oil shale deposits in Colorado is moving ahead on a firm basis, with two federal lease tracts (C-a and C-b) beginning mine excavation work this year, and demonstration retorts already operating at Anvil Points (Paraho) and Logan Wash (Occidental Oil Shale). First production runs are expected to take place at the federal lease tracts in the early 1980's. With this activity in motion, the U.S. EPA began an environmental assessment program of shale oil recovery processes over two years ago.

The characterization of oil shale processes has been difficult and speculative without having a full-scale industry in being. Nevertheless, the need is urgent for an understanding of the kind of pollution control needs that will be faced by the new industry.

The Paraho Process

Arrangements were made in 1976 to conduct environmental sampling and analysis at the Paraho demonstration site at Anvil Points, CO. The test plan was quickly put into action, since the demonstration plant was about to conclude a 30-month program.

The demonstration plant operations, indicated schematically in Figure 1, consisted of mining, raw shale hauling, crushing and screening, retorting, and retorted shale disposal. Crude shale oil was stored in tanks for subsequent shipment to an off-site refinery. The heart of the demonstration plant is the Paraho retort (Figure 2), which can process about 400 metric tons per day.

Provision has been made for operating the retort in either the direct mode or indirect mode. In the direct mode the carbon on the retorted shale is burned in the combustion zone to provide the principal fuel for the process. Low calorie retort gases are recycled to both the combustion zone and the gas preheating zone. In the indirect mode heat for retorting is supplied by recycling off-gases through an external furnace, thus eliminating combustion in the retort and producing a high heating value, 8000 kcal/std cu meter off-gas.

In either mode of operation, raw shale is fed into the top of a Paraho retort and passed downward by gravity successively through a mist formation and preheating zone, a retorting zone, either a combustion zone (direct mode) or heating zone (indirect mode), and finally, a residue cooling and gas preheating zone. It is discharged through a hydraulically-operated grate, which controls the throughput rate and maintains even flow across the retort. The retorted shale is discharged from the retort at about 150°C (300°F), and sent to the shale disposal area.

The shale vapors produced in the retorting zone are cooled to a stable mist by the incoming raw shale (which is thereby preheated), and leave the retort. This mist is sent to a condenser, and finally a wet electrostatic precipitator, for oil separation. The resulting shale oil is transported to storage.

The demonstration plant differs considerably from a commercial facility design, so that it cannot be considered a scale model of a full-size operation. The product gas at the demonstration plant was combusted in a thermal oxidizer prior to atmospheric discharge; in a commercial facility, this gas would be cleaned and used as a fuel in process heaters and boilers. Material handling in a commercial plant would most likely rely on conveyors, rather than trucks, and the disposal of retorted shale would be a major portion of the operation.

Sampling Methodology

Sampling methods, equipment, and stations were specific to the nature of the specie monitored Multi-media sampling approaches included

- Proportional and grab sampling of the recycle process gas stream and thermal oxidizer discharge for analysis by instrumental and wet chemical methods.
- Grab sampling of the product crude oil, recycle process gas condensate water, and retorted shale for organic and trace element analysis.
- Grab sampling of recycle process gas stream condensate water for gross parameter analysis—for example, biochemical oxygen demand,

chemical oxygen demand, total organic carbon and pH.

- High-volume sampling of particulate emissions from raw shale mining, crushing, and retorted shale transfer.
- Cascade impactor sampling for particulate sizing of airborne emissions from raw and retorted shale processing.

Standard EPA sampling procedures for ambient or stack monitoring were modified as necessary to be usable in a process environment. This required, for example, sample train impinger solutions to be at much higher concentrations for recycle gas sampling, in order to avoid incomplete capture of high-concentration constituents in the gas stream. Collection of fugitive dust in close proximity to shale-handling equipment was done with high-vol sampler durations of less than an hour. Bulk retorted shale samples, taken fresh from the retort discharge conveyor, were immediately capped, since the volatile emissions from retorted shale were as much of interest as the solid material. Preservation methods for shale oil process condensates must be carefully selected to prevent modification of the constituents. Freezing was eventually determined to be the best method.

Sample Processing and Analysis

The initial sampling and analysis program was conducted at the Paraho facility in 1976, shortly before the plant was scheduled to shut down. Therefore the analysis effort went considerably beyond the Level 1 approach (1), since there was no opportunity to conduct a follow-up effort at the time. (A resumption of operations in 1977 afforded the chance for a second test effort).

Standard analytical methods were used wherever possible. Specific techniques were developed to handle some of the various process samples. Figures 3, 4, and 5 show plans for processing and analysis of the Paraho gaseous, liquid, and solid samples. Analytical methods included

- Inorganic and trace elements analysis
  - —wet chemistry
  - —atomic absorption spectrophotometry
  - —gas chromatography
  - —spark source mass spectrometry (SSMS)
- Organic analysis, separation and identification with
  - —gas chromatography (GC)/mass spectrometry (MS)
  - —thin layer chromatography (TLC)
  - —high-pressure liquid chromatography (HPLC) and Level 1 LC methods
  - —spectrophotofluoremetry (SPF)
- Polynuclear aromatic hydrocarbons analysis —two-dimensional elution with TLC.
- Particulate size analysis by gravimetric determinations of impactor fractions, and scanning electron microscopy of low-volume sampler filters.

Although a detailed description of the analysis methods are available in a separate publication (2), some particular characteristics of shale oil process stream analysis can be highlighted. Recycle gas condensates and aqueous samples from crude oil/water separation must have the oily and aqueous phases separated under standard conditions to obtain reproducible results. Organic components were typically 0.2 - 0.3 wt. percent, including acids, bases, and neutrals (primarily aromatics). Inorganic constituents were chiefly ammonium carbonate and bicarbonate, although a wide variety of trace elements were found in small quantities. (Trace elements contained in oil shale appear to be mostly retained in retorted shale, with some carryover to the crude shale oil). The presence of a high concentration of ammonia interferred with standard titrimetric determinations for carbonate and bicarbonate alkalinity, so that inference from total inorganic carbon was used.

Ammonia was also found in the recycle gas stream at about 1 volume percent levels, along with hydrogen sulfide (in the 0.1 volume percent range). These constituents would be removed in a gas-cleaning unit under full-scale operations. Emissions from burning the treated gas would then be similar to natural gas combustion.

Considerable extraction and separation of inorganic and organic components from solid samples was done, using both bulk retorted shale and airborne particulate samples. Classification was done in the case of particulates for organic components separated by Level 1 liquid chromatography. Retorted shale was singled out for thin layer chromatography analysis, in order to determine the ratio of polynuclear aromatics to polar compounds (about 50/50 by wt. in retorted shale, 15/85 in raw shale particulate matter).

Implications for Future Environmental Work

Modular and full-scale shale oil plants will have to be monitored for a number of atmospheric and aqueous waste constituents. Automatic measurement techniques will have to be developed, to avoid the cost of manual sampling and laboratory analyses. Sampling and analysis programs such as this one serve to characterize various constituents found in process and waste streams, but do not answer the question of monitoring priorities. Health effect studies, comparison with natural environment characteristics, and studies of residual behavior are all needed to determine priorities of concern. For example, the interaction of retorted shale with water from natural sources or process wastewater needs to be understood before groundwater monitoring programs can be well designed.

The same comments apply to the development of appropriate pollution control technologies, since only a few of the constituents found in shale oil by-product streams are covered by existing federal or state regulations. The development and improvement of oil shale retorting processes needs to be done in parallel with pollution control evaluation, since process methodologies will affect the characteristics and quantities of waste streams.

Finally, characterizations of shale oil product uses will be needed. Combustion of crude shale oil has been monitored in one case (3), and future work should examine the impacts of refined product consumption.

References

(1) IERL-RTP Procedures Manual: Level 1 Environmental Assessment, EPA-600/2-76-160a, June 1976

(2) Sampling and Analysis Research Program at the Paraho Shale Oil Demonstration Plant, IERL-Ci, to be published (TRW Contract 68-02-1881, May 1977)

(3) D. G. Jones, M.N. Mansour, Low NO_x Combustion of Paraho Shale Oil in a 45 MW Utility Boiler, ASME 77-WA/Fu-1, Atlanta, December 1977

Figure 1. Anvil Points operations.

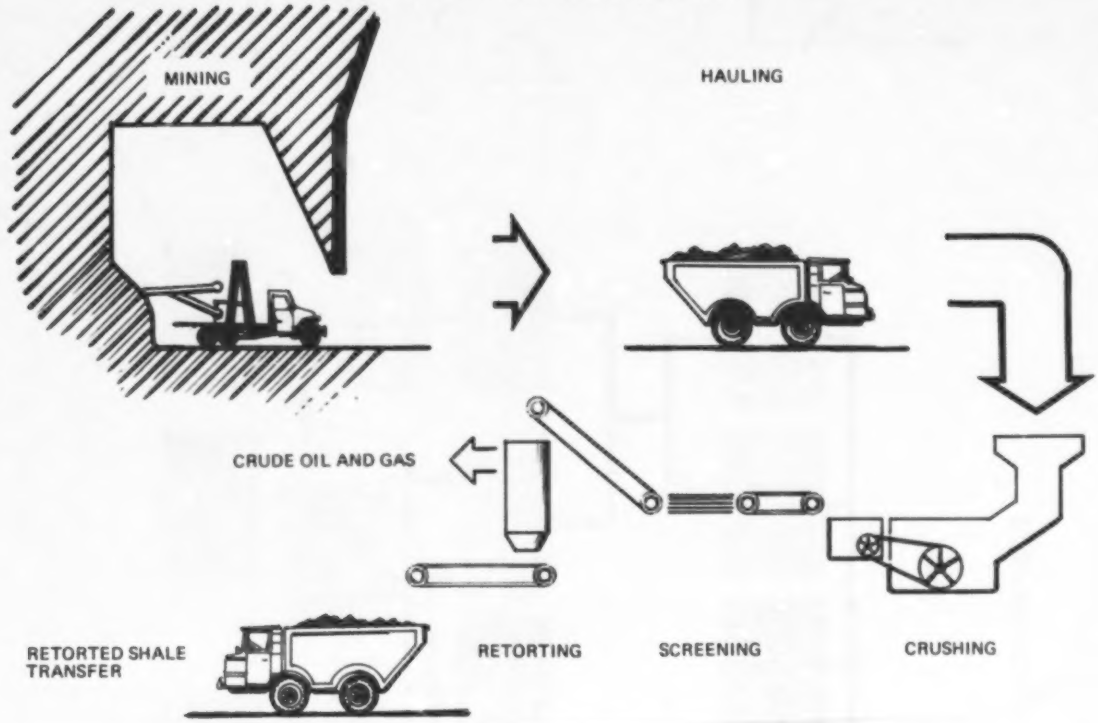

MINING
HAULING
CRUDE OIL AND GAS
RETORTED SHALE TRANSFER
RETORTING
SCREENING
CRUSHING

Figure 2
PARAHO RETORTING, INDIRECT MODE

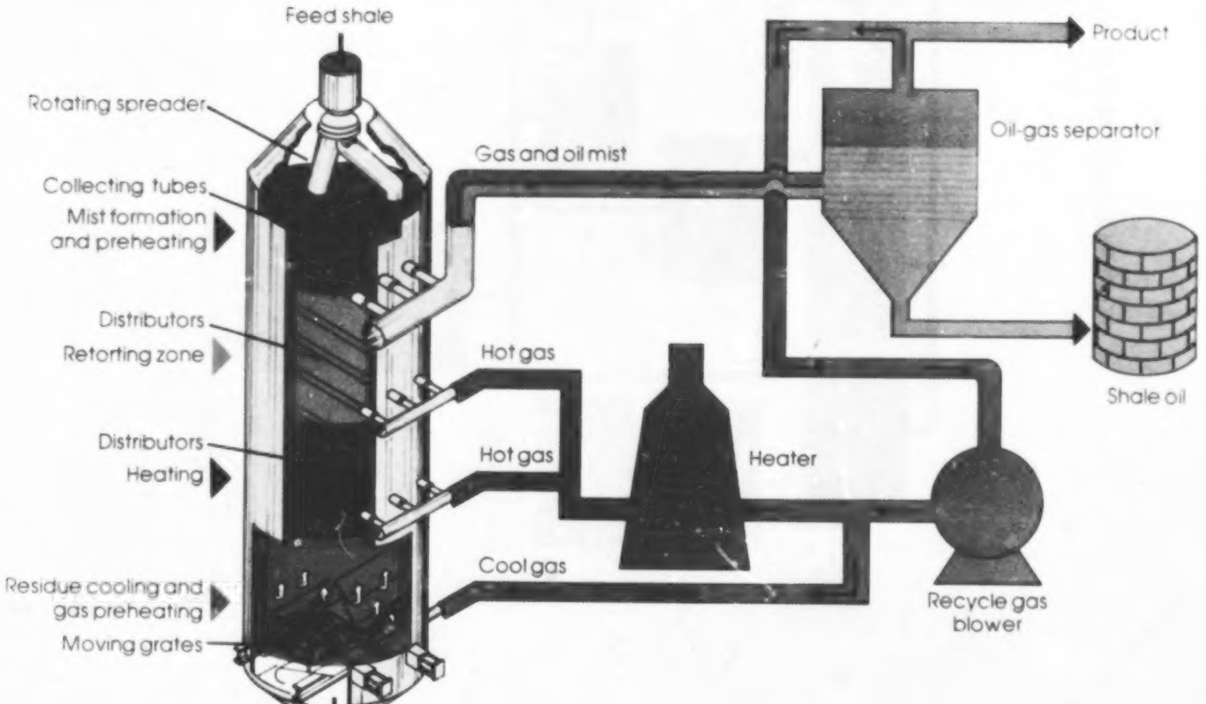
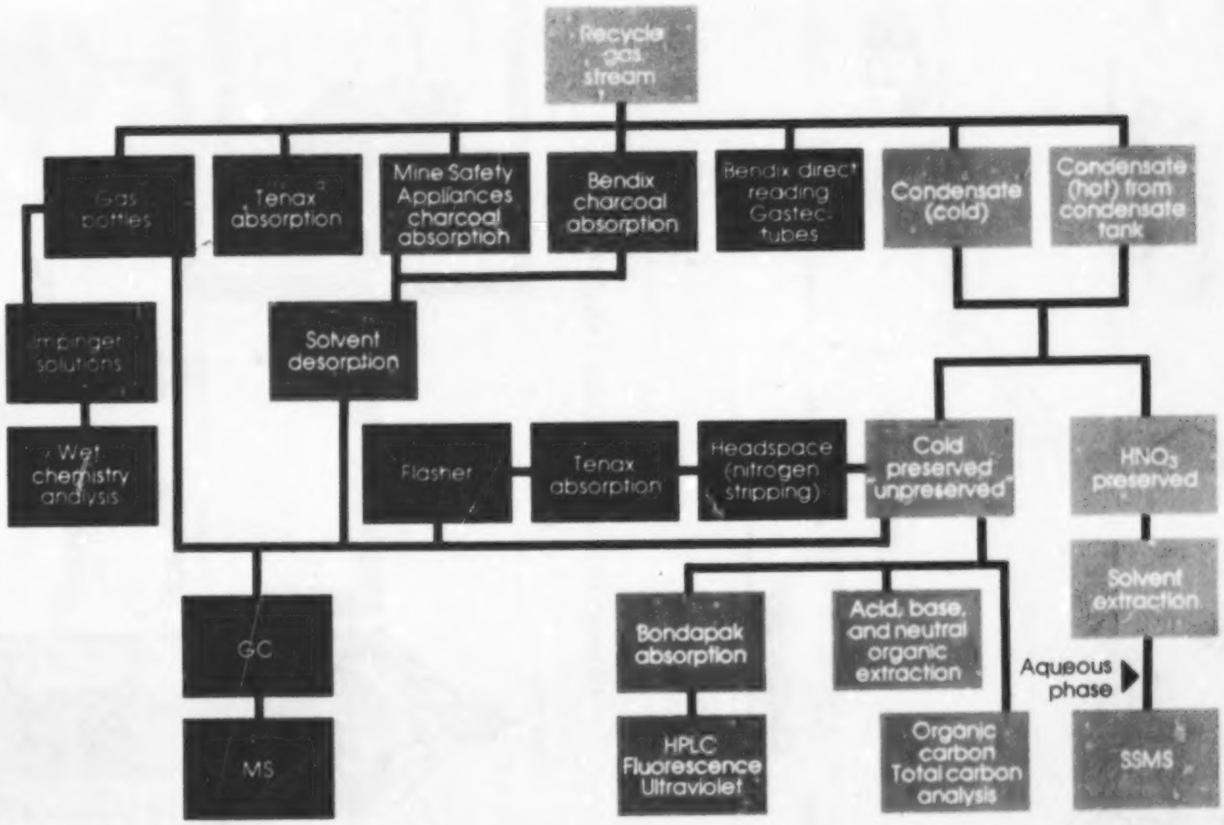
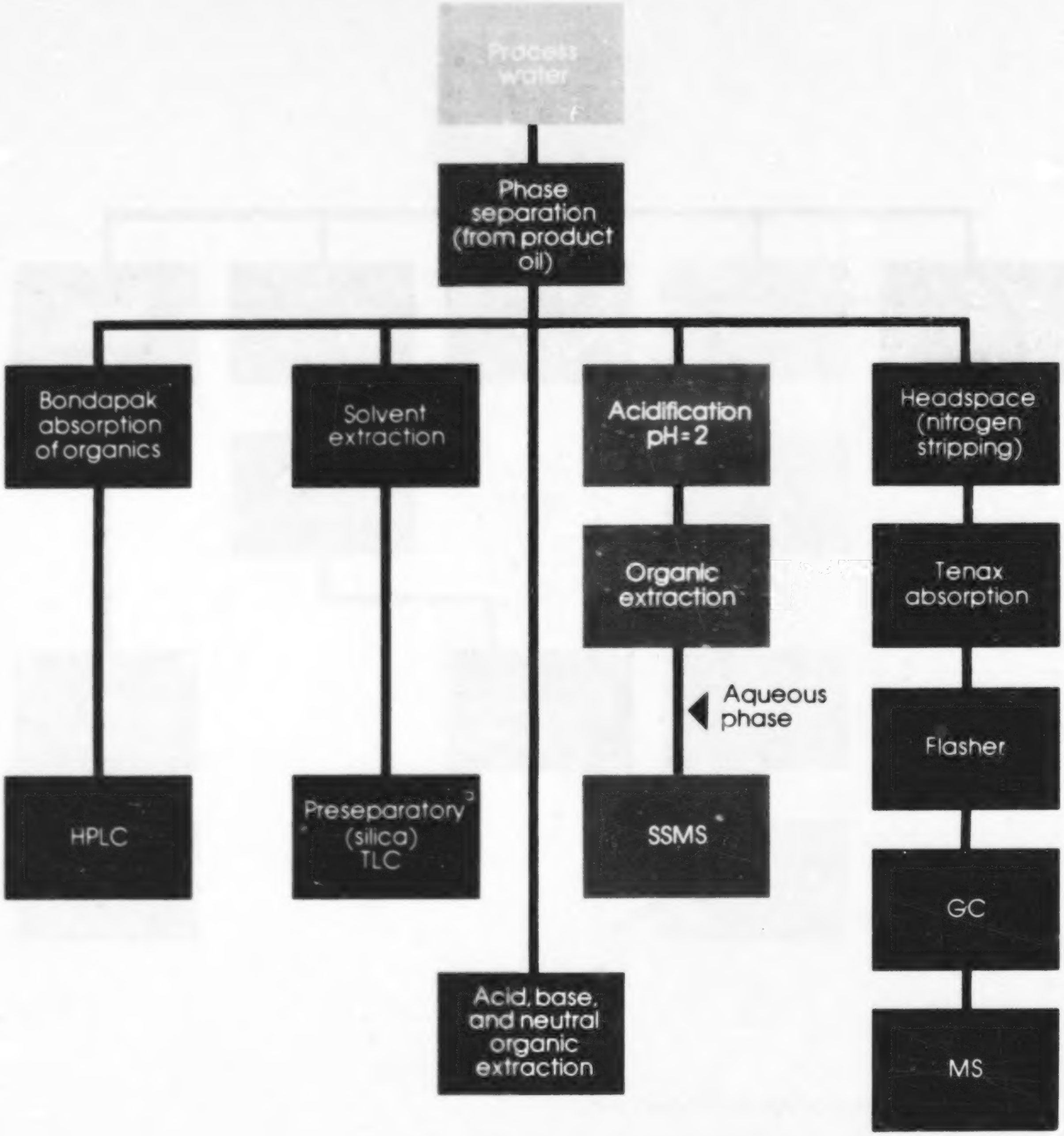

Feed shale
Product
Rotating spreader
Oil-gas separator
Gas and oil mist
Collecting tubes
Mist formation and preheating
Shale oil
Distributors
Retorting zone
Hot gas
Distributors
Hot gas
Heater
Heating
Cool gas
Residue cooling and gas preheating
Recycle gas blower
Moving grates
Retorted shale to disposal beds

Figure 3
SEPARATION AND ANALYSIS SCHEME, GASEOUS SAMPLES


Recycle gas stream
Gas bottles
Tenax[a] absorption
Mine Safety Appliances charcoal absorption
Bendix charcoal absorption
Bendix direct reading Gastec tubes
Condensate (cold)
Condensate (hot) from condensate tank
Impinger solutions
Wet chemistry analysis
Solvent desorption
Flasher
Tenax absorption
Headspace (nitrogen stripping)
Cold preserved "unpreserved"
HNO3 preserved
Solvent extraction
Aqueous phase
SSMS
GC
MS
Bondapak absorption
HPLC Fluorescence Ultraviolet
Acid, base, and neutral organic extraction
Organic carbon Total carbon analysis

[a] Not used because of the presence of aerosol.

Figure 4
SEPARATION AND ANALYSIS SCHEME, WATER SAMPLES


Process water
Phase separation (from product oil)
Bondapak absorption of organics
Solvent extraction
Acidification pH = 2
Headspace (nitrogen stripping)
Organic extraction
Tenax absorption
Aqueous phase
Flasher
HPLC
Preseparatory[a] (silica) TLC
SSMS
GC
Acid, base, and neutral organic extraction
MS

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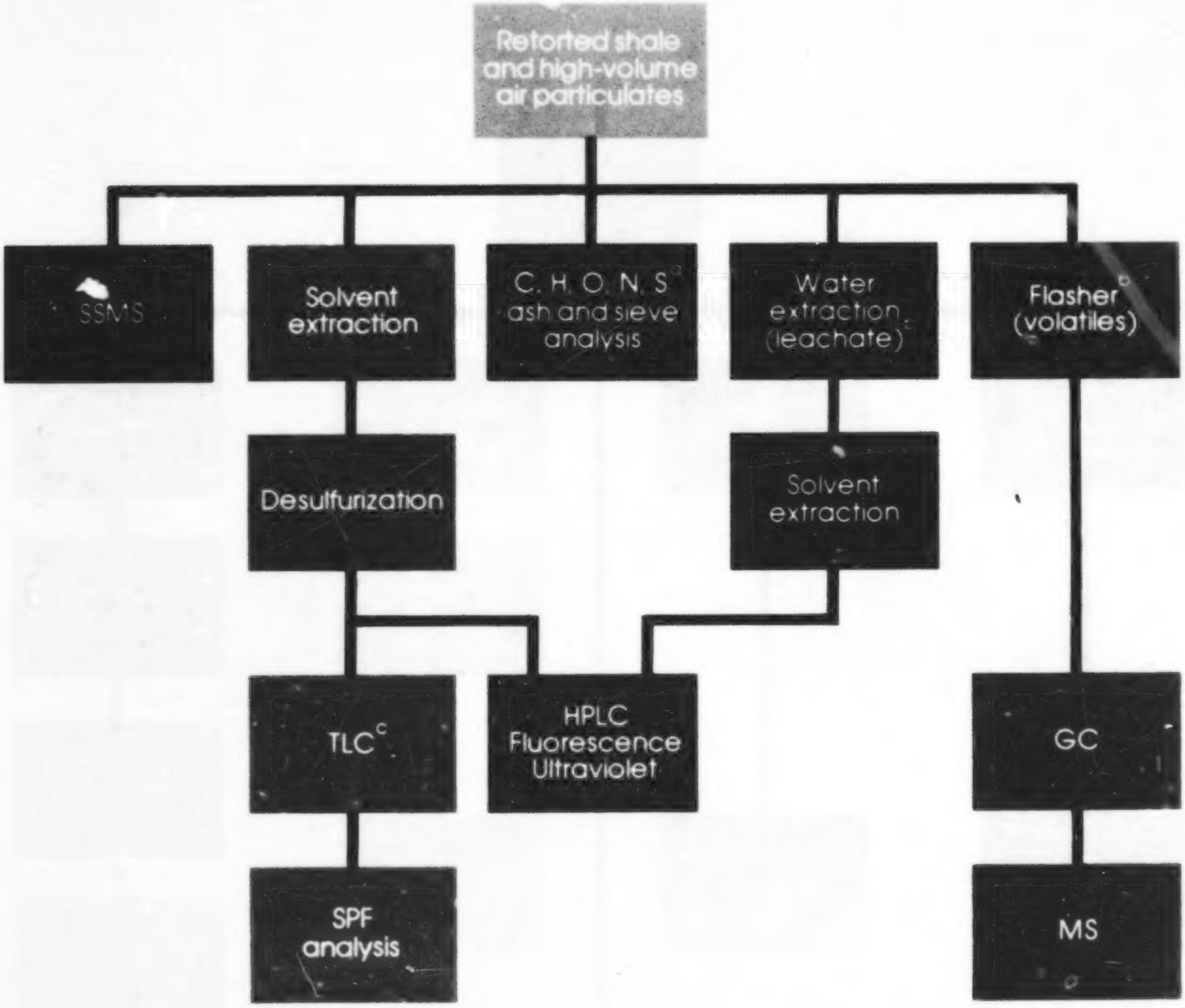
[a] TLC analytical scheme.

Figure 5
SEPARATION AND ANALYSIS SCHEME,
RETORTED SHALE AND HIGH-VOLUME SAMPLER AIR PARTICULATES



Retorted shale and high-volume air particulates
SSMS
Solvent extraction
C, H, O, N, S[a] ash and sieve analysis
Water extraction (leachate)
Flasher[b] (volatiles)
Desulfurization
Solvent extraction
TLC[c]
HPLC Fluorescence Ultraviolet
GC
SPF analysis
MS

[a] Carbon, hydrogen, oxygen, nitrogen, sulfur.

[b] Not performed on air particulates.

[c] TLC analytical scheme.